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A NEW EFFECT OF HYDROGEN BOND FORMATION (CHELATION)

Part VII. Hydrogen Peroxide Oxidation of Some 2′-Substituted Chalkones and Flavanones

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(From the Department of Chemistry, Delhi University)

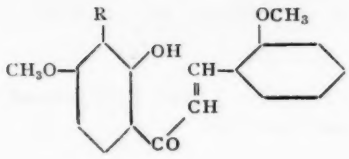
Received December 18, 1952

In our previous communications[1, 2] were reported the extraordinary properties of 2′-hydroxy and methoxy flavanones and 2′-methoxy chalkones. In view of these features and particularly because of the failure to convert the 2′-hydroxy and methoxy flavanones into flavones by iodine and sodium acetate[2] it was considered necessary to study the reaction of these compounds towards alkaline hydrogen peroxide. Further the conversion of chalkones to known derivatives of flavonols would add support to their constitutions. The results obtained in the course of this study are recorded in this paper.

It has already been pointed out[3] that chalkones without a substituent in the 6-position yield flavonols on oxidation with hydrogen peroxide while a substituent in this position causes the formation of benzal-coumaranones. The behaviour of 2′-methoxy chalkones is in agreement with this generalisation. Thus 2-hydroxy-4 : 2′-dimethoxy chalkone (I *a*) and 2-hydroxy-3 : 4 : 2′-trimethoxy chalkone (I *b*) give rise to the expected 7 : 2′-dimethoxy (II *a*) and 7 : 8 : 2′-trimethoxy (II *b*) flavonols. The former (II *a*) on methylation yields the trimethyl ether recently reported by Jain *et al.*[4] The products in these cases are exclusively flavonols as shown by their complete solubility in aqueous sodium hydroxide and positive ferric reaction.

Similar oxidation of 2-hydroxy-6 : 2′-dimethoxy chalkone (III *a*), and 2-hydroxy-4 : 6 : 2′ : 4′-tetramethoxy chalkone (III *b*) yields the corresponding benzal-coumaranones (IV *a* and IV *b*). The products separate from the alkaline solution, give no colour with ferric chloride and develop a deep red colour with concentrated sulphuric acid.

A very different result is obtained when the 2′-hydroxy flavanones are treated under the same conditions with alkaline hydrogen peroxide. 5-Methoxy-2′-hydroxy, 5 : 7-dimethoxy-2′-hydroxy and 5 : 7 : 4′-trimethoxy-2′-hydroxy flavanones remain unaffected and are recovered completely unchanged. Variations in the strength of alkali or quantities of hydrogen peroxide used have no effect. In this resistance to oxidation the influence of the 2′-hydroxyl in the flavanone seems to be similar to that of the 5-hydroxyl



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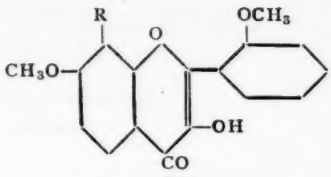

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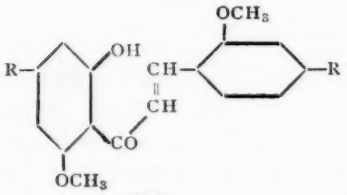

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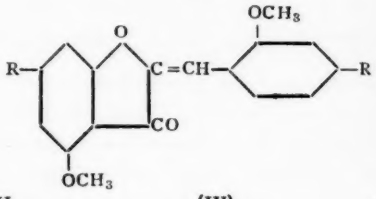


(IV)

a, R = H
b, R = OCH_3

group, for under the same conditions 5-hydroxy-2′-methoxy flavanone and naringenin-7 : 4′-dimethyl ether are also recovered unchanged after treatment with alkaline hydrogen peroxide.

A possible explanation for the absence of oxidation in the case of these 2′- and 5-hydroxy flavanones seems to be in their stability and their inability to change into the chalkone form. The work of Reichel and Steudel[5] definitely shows that ordinary flavanones are unaffected by alkaline hydrogen peroxide and it is only after conversion to the chalkones that the reagent is able to have any action. But the remarkable feature is that whereas these flavanones unsubstituted in the pyrone nucleus are unreactive and do not give even the flavones, the corresponding 3-hydroxy flavanones, which have been shown to be intermediates by Reichel and Steudel[5] in the formation of flavanols from chalkones, undergo dehydrogenation readily in the presence of the hydrogen peroxide or air. Obviously a hydroxyl substituent in the 3-position plays an important part in the mechanism of further oxidation. Similar observations have been made regarding 3-hydroxy flavanones occurring in nature. Pew[6] recorded that 3-hydroxy naringenin and 3-hydroxy eriodictyol underwent ready dehydrogenation even by air. Similar results have been obtained in our laboratories in the course of our work on this group of compounds.

EXPERIMENTAL

7 : 2′-*Dimethoxy-flavonol* (*II a*)

2-Hydroxy-4 : 2′-dimethoxy chalkone (I *a*) required for this reaction was made from equimolecular proportions of peonol and *o*-methoxy benzaldehyde using the sodium ethoxide method.[1] It was obtained in a semi-solid

form and could not be crystallised and was used as such for the oxidation. An ice-cooled solution of the chalkone (1 g.) in aqueous hydroxide (20 c.c.; 2N) was treated with hydrogen peroxide (5 c.c.; 15%) during the course of 5 minutes and the solution left in the ice-bath for 2 hours. The dark coloured solution was then acidified with hydrochloric acid (ice-cold 1 : 1) and directly extracted with ether. The ether solution was dried over sodium sulphate, the ether distilled off and the residue dissolved in a mixture of hot ethyl acetate and petrol. A pale yellow solid gradually separated on cooling the solution. It crystallised from alcohol as pale yellow aggregates of thin rectangular plates melting at 158–60°. It gave a brown colour with ferric chloride in alcoholic solution and was easily soluble in aqueous sodium hydroxide (Found: C, 66·7; H, 5·3; $C_{17}H_{14}O_5$, $\frac{1}{2}H_2O$ requires C, 66·5; H, 4·9%).

3 : 7 : 2′-*Trimethoxy flavone* (*resodatiscetin trimethyl ether*)

The above flavonol (0·2 g.) was methylated with excess of dimethyl sulphate (0·2 c.c.) and anhydrous potassium carbonate (1 g.) in acetone solution. The methyl ether crystallised from alcohol as colourless prisms melting at 135–6°, was identical with an authentic sample of 3 : 7 : 2′-trimethoxy flavone[4] and a mixed melting point with that sample was undepressed.

7 : 8 : 2′-*Trimethoxy flavonol* (*II b*)

2-Hydroxy-3 : 4 : 2′-trimethoxy chalkone (I *b*)[1] (0·5 g.) was oxidised with hydrogen peroxide (3 c.c.; 15%) in sodium hydroxide solution (15 c.c.; 2N) and alcohol (10 c.c.) under conditions described in an earlier experiment. After leaving overnight the alkaline solution was acidified and the yellow solid that separated was filtered, washed with water and crystallised from alcohol. It separated in the form of yellow stout rectangular prisms melting at 107–8°. It gave a brown colour with ferric chloride, yellow colour with concentrated sulphuric acid and was soluble in aqueous sodium hydroxide (Found: C, 66·2; H, 5·3; $C_{18}H_{16}O_6$ requires C, 65·8; H, 4·9%).

4 : 2′-*Dimethoxy benzalcoumaranone* (*IV a*)

2-Hydroxy-6 : 2′-dimethoxy chalkone (III *a*)[1] (1·0 g.) was dissolved in alcohol (10 c.c.) and sodium hydroxide (15 c.c.; 2N) and the cooled solution treated with hydrogen peroxide (5 c.c.; 15%). A bright yellow solid began to separate out after 2 hours. The mixture was left in the refrigerator overnight and the solid that separated was filtered and washed with water. Dilution of the filtrate gave more of the solid. On crystallising from alcohol the product separated as bright yellow elongated rectangular rods and prisms melting at 203–4°. Yield 0·6 g. It gave no colour with ferric

chloride and with concentrated sulphuric acid developed a bright red colour thus agreeing with the requirements of the benzalcoumaranone structure. Acidification of the alkaline filtrate gave no solid product (Found: C, 72·1; H, 5·1; $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%).

4:6:2′:4′-*Tetramethoxy benzalcoumaranone* (*IV b*)

2-Hydroxy-4:6:2′:4′-tetramethoxy chalkone (III *b*)[1] (1·0 g.) was oxidised under the same conditions using the same quantities of reagents as in the previous experiment and the product worked up. It crystallised from alcohol as yellow rectangular prisms melting at 172–4°. It gave no colour with ferric chloride but with concentrated sulphuric acid gave a deep red colour (Found: C, 66·2; H, 5·7; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%).

Action of alkaline hydrogen peroxide on 2′-hydroxy and 5-hydroxy flavanones

The following flavanones were used for the reaction under the various experimental conditions: (i) 5-methoxy-2′-hydroxy flavanone,[1] (ii) 5:7-dimethoxy-2′-hydroxy flavanone,[1] (iii) 5:7:4′-trimethoxy-2′-hydroxy flavanone,[1] (iv) 5-hydroxy-2′-methoxy flavanone,[2] and (v) 5-hydroxy-7:4′-dimethoxy flavanone.[7] The experimental conditions are given below:

(*a*) The flavanone (0·5 g.) was dissolved in alcohol (10 c.c.) and aqueous sodium hydroxide (15 c.c.; 10%) and the solution cooled in ice-water. It was then treated with aqueous hydrogen peroxide (5 c.c.; 15%) and left overnight in the refrigerator. Acidification of the solution deposited a colourless solid which was filtered, washed with water and crystallised from alcohol.

(*b*) The quantities of both sodium hydroxide and hydrogen peroxide were doubled and the reaction mixture was left overnight at room temperature.

(*c*) The flavanone (0·5 g.) was dissolved in alcohol (10 c.c.) and aqueous sodium hydroxide (15 c.c.; 10%) and the solution was treated with a much stronger hydrogen peroxide (5·0 c.c.; 30%) at 0°. After standing in the refrigerator for 24 hours it was worked up as in experiment (*a*).

(*d*) This was carried out only with naringenin dimethyl ether.[7] It (0·5 g.) was dissolved in sodium hydroxide (10 c.c.; 10%) and a minimum amount of pyridine to give a clear solution and the mixture treated with hydrogen peroxide (5 c.c.; 30%) at 0°.

In all the cases it was found that the compounds were recovered unchanged from the reaction. They were identified by their colour reactions, crystal structures, melting points and mixed melting points with authentic

samples of the original compounds. There was hardly any appreciable loss of the flavanones during the treatment with hydrogen peroxide.

Summary

In their behaviour towards alkaline hydrogen peroxide 2′-methoxy chalkones behave normally and yield flavonols if the 6-position is free and benzalcoumaranones if this position has a methoxyl group. On the other hand 2′-hydroxy flavanones and 5-hydroxy flavanones remain unaffected. This result is explicable on the basis that these hydroxy flavanone structures are stable and do not undergo change into the corresponding chalkone structures which alone suffer oxidation.

References

1. Narasimhachari, Rajagopalan and Seshadri .. *Proc. Ind. Acad. Sci.*, 1952, **36A**, 231.
2. ———— .. *Ibid.*, 1953, **37A**, 620.
3. Geissman and Fukushima .. *J.A.C.S.*, 1948, **70**, 1686.
   Balakrishna *et al.* .. *Proc. Ind. Acad. Sci.*, 1949, **30A**, 120.
   Narasimhachari and Seshadri .. *Ibid.*, 1949, **30A**, 216.
4. Jain *et al.* .. *Ibid.*, 1952, **36A**, 217.
5. Reichel aad Steudel .. *Ann.*, 1942, **553**, 83.
6. Pew .. *J.A.C.S.*, 1948, **70**, 3031.
7. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1948, **28A**, 223.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXX. A New Synthesis of Hydroxy Xanthones Including Gentisein and Gentisin

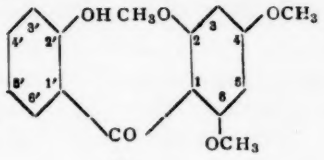
By G. Venkat Rao and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Delhi University)

Received January 17, 1953

For the synthesis of the xanthone structure a number of methods have been used. The earliest was that employed by Kostanecki[1] in which he distilled an intimate mixture of a phenol and *o*-hydroxy benzoic acid with acetic anhydride as the condensing agent. By this method Kostanecki synthesised numerous hydroxy xanthones. However the yields were very poor and the method of working up the product was very tedious. Later Ullmann[2] developed a method in which the diphenyl ether linkage was first built and subsequent ring closure effected using various condensing agents such as concentrated sulphuric acid, anhydrous aluminium chloride and phosphorus oxychloride. A third method used by Robinson and Nishikawa[3] consists of the Hoesch condensation of *o*-hydroxy benzonitrile and a phenol in dry ether in presence of zinc chloride and hydrogen chloride. A ketimine hydrochloride is formed which on alkaline hydrolysis yields directly the xanthone. But these methods are not available easily for all cases. Consequently there was need to explore new routes to the synthesis of xanthone derivatives. The Friedel and Craft's reaction in its simple form has not so far been employed for this purpose. As a simple example of the application of this reaction salicylic acid monomethyl ether and phloroglucinol trimethyl ether are now employed. The acid chloride of the former is condensed with the latter in the presence of anhydrous aluminium chloride in cold dry ether solution. The reaction proceeds satisfactorily and a good yield of a ketone is obtained. The product gives colour with alcoholic ferric chloride solution and analysis indicates that one methoxyl group has suffered demethylation. There are two possibilities for its structure (I and II *a*). In order to settle this question the ethyl ether of salicylic acid has also been used for this condensation. This product is different from the first one and analysis shows that the ethyl group is retained. Hence it could be concluded that the ortho methoxyl which suffers demethylation belongs to the phloroglucinol part (2-position) and the structure of the products is

correctly represented by (II *a* and *b*). Subsequent treatment of the trimethyl ether (II *a*) with anhydrous aluminium chloride in boiling benzene gives rise to a good yield of 1 : 3-dihydroxy xanthone (III), which on methylation with excess of dimethyl sulphate in acetone solution provides the dimethyl ether.



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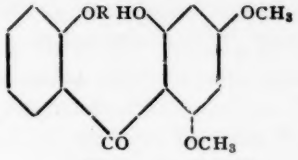
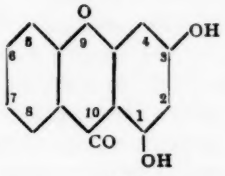
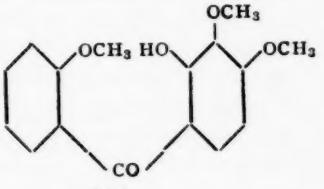


(II) *a*, R=CH_3
b, R=C_2H_5



(III)

The above mentioned reaction has been carried out using *o*-methoxy benzoyl chloride and pyrogallol trimethyl ether and a good yield of 3 : 4-dihydroxy xanthone (V) has been obtained.



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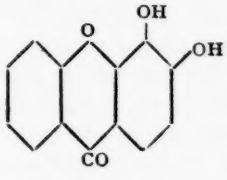
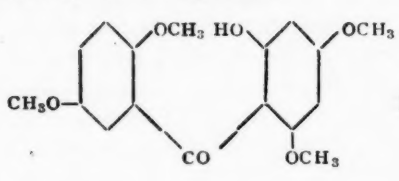


(V)

The method has next been employed for the synthesis of gentisein (VI *a*) and its naturally occurring monomethyl ether gentisin. Gentisin (VI *b*), the yellow colouring matter of *Gentiana lutea* (gentian root) was shown by Kostanecki[4] to be a monomethyl ether of gentisein, 1 : 3 : 7-trihydroxy xanthone which was synthesised by the distillation of a mixture of gentisic acid, phloroglucinol and acetic anhydride.[5] He obtained gentisin itself by the partial methylation of gentisein[5] (yield not stated). This synthesis was at that time not considered to be definite proof of its constitution. In view of recent analogies it should be taken as establishing the constitution of gentisin as the 3-methyl ether of gentisein. However, the point was unequivocally established by Shinoda's synthesis[6] of gentisein 7-methyl ether which was different from gentisin. The possibility of gentisin being the

1-methyl ether of gentisein was eliminated even earlier since methylation of gentisin with excess of methyl iodide did not yield a dimethyl ether but gave only a monomethyl ether. The constitution has been further confirmed by the recent work of Anand and Venkataraman[7] who prepared 7-nitro-1-hydroxy-3-methoxy xanthone and converted the nitro group into the hydroxyl by conventional methods.

The present synthesis consists of the condensation of 2: 5-dimethoxy benzoyl chloride with phloroglucinol trimethyl ether. The 2-hydroxy-4: 6: 2′: 5′-tetramethoxy benzophenone (VII) obtained as the intermediate undergoes easy conversion into gentisein (VI *a*), either by treatment with aluminium chloride in boiling benzene solution or with boiling hydriodic acid in acetic anhydride solution. The preparation of gentisin (VI *b*) has now been done by the partial methylation of gentisein (VI *a*) using 1 mole of dimethyl sulphate in acetone solution in the presence of anhydrous potassium carbonate. The partial methylation yields mainly gentisin (VI *b*), since the 3-hydroxyl in (VI *a*) is the most acidic and reactive. It corresponds to the 7-hydroxyl in chromones and is influenced by the C = O group in the para position,[8] whereas the 7-hydroxyl in xanthones is not so affected and the 1-hydroxyl is protected by chelation. There is however some unchanged gentisein, and the mixture is separated by using difference in solubilities in sodium carbonate and sodium hydroxide solutions. Unreacted gentisein dissolves in aqueous sodium carbonate by virtue of the 3-hydroxyl group which is markedly acidic (see formula VI *a*). The sodium hydroxide soluble portion gives a good yield of gentisin. There is no detectable amount of the dimethyl ether. Gentisin has also been obtained by the partial demethylation and simultaneous ring closure of 2-hydroxy-4: 6: 2′: 5′-tetramethoxy benzophenone (VII) using hydriodic acid at 110°. The principle of this reaction has already been discussed in connection with isoflavone derivatives.[9, 10] In this reaction the trimethoxy xanthone should be first formed and the more easily susceptible 1 and 7-methoxyl groups undergo preferential demethylation, the more stable 3-methoxyl remaining behind.



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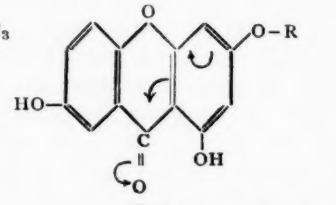

(VI) *a*, R=H
b, R=CH_3

Experimental

1 : 3-*Dihydroxy xanthone* (*III*)

(*a*) 2-*Hydroxy*-4 : 6 : 2′-*trimethoxy benzophenone* (*II a*).—Freshly powdered anhydrous aluminium chloride (12 g.) was dissolved in dry ether (100 c.c.) with cooling in ice, and to the solution was added phloroglucinol trimethyl ether (4·2 g.). The mixture was cooled for fifteen minutes, after which time freshly distilled *o*-methoxy benzoyl chloride (5 c.c.) was added in small quantities during half an hour with occasional shaking. Only after the addition of the acid chloride was complete a dark brown oily complex separated and the reaction mixture was allowed to stand at the temperature of the laboratory for 48 hours. It was then treated with crushed ice and concentrated hydrochloric acid (25 c.c.), and the ether distilled off on a water-bath. Benzene (50 c.c.) was then added and the mixture refluxed for half an hour on a water-bath. The benzene layer was separated while still hot and the aqueous solution extracted once again with benzene (50 c.c.). The combined benzene extract was washed with water and dilute sodium bicarbonate solution (5%) and the solvent distilled off when an oily product was obtained which solidified on cooling. It crystallised from methanol as stout rhombohedrons melting at 92–3°; yield, 4·5 g. (Found: C, 66·8; H, 6·0; $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%).

The benzophenone is insoluble in cold alkali but dissolves in hot alkali giving rise to an yellow solution which on cooling deposits a pale yellow solid. It gives a deep red colour with alcoholic ferric chloride. With concentrated nitric acid it gives a deep blue colour which changes on standing to dirty green and finally purple. It dissolves in concentrated sulphuric acid to an yellow solution which develops a bluish green fluorescence on standing.

(*b*) *Demethylation and ring closure.*—The above benzophenone (1·25 g.) was dissolved in dry benzene (50 c.c.), freshly powdered anhydrous aluminium chloride (8 g.) was added and the mixture shaken for a few minutes when a dark reddish brown complex separated. The mixture was refluxed on a water-bath for 2 hours and the solvent distilled off. The oily residue was cooled and the complex decomposed by treatment with crushed ice and concentrated hydrochloric acid (15 c.c.), and warming in a water-bath for 10 minutes. The mixture was extracted with ether thrice (50 c.c. each time). The combined ether extract was then washed with sodium carbonate solution thrice (10% solution; 20 c.c. each time). On acidifying the alkaline extract with concentrated hydrochloric acid a gelatinous mass was obtained which coagulated on heating. This was filtered, dried and crystallised from dilute alcohol when 1 : 3-dihydroxy xanthone was obtained as aggregates of colourless rectangular prisms and needles melting at 256–8°[3] yield, 0·3 g. The

substance answers all the colour reactions recorded in the literature[3] for 1 : 3-dihydroxy xanthone. It dissolved in sodium carbonate solution giving a deep yellow colour.

The diacetate of the xanthone was obtained by boiling with acetic anhydride and freshly fused sodium acetate. It crystallised from alcohol as colourless elongated rectangular prisms melting at 145°.[1]

1 : 3-*Dimethoxy xanthone*

The dihydroxy xanthone (0·25 g.) was dissolved in dry acetone (50 c.c.), redistilled dimethyl sulphate (1 c.c.) and ignited potassium carbonate (2 g.) added and the mixture refluxed on a water-bath for 48 hours. The acetone solution was filtered hot and the potassium salts washed with hot acetone. The solvent was distilled off and the residue dissolved in ether. The ether solution was washed with dilute alkali (in order to remove any partial methyl ether). The solvent was distilled off and the residue crystallised from dilute alcohol when it came out as long silky needles melting at 167–9° (Found: C, 61·7; H, 5·7; $C_{15}H_{12}O_4\ 2H_2O$ requires C, 61·5; H, 5·7%). It dissolved in concentrated sulphuric acid to give an yellow solution which developed a greenish blue fluorescence on standing.

2-*Hydroxy*-4 : 6-*dimethoxy*-2′-*ethoxy benzophenone* (*II b*)

o-Ethoxy benzoyl chloride (5 c.c.) and phloroglucinol trimethyl ether (4·2 g.) were condensed in the presence of anhydrous aluminium chloride (12 g.) in dry ether solution (100 c.c.). The reaction was carried out as mentioned earlier. The benzophenone crystallised from alcohol as straw yellow rectangular prisms melting at 160–1°; yield, 4 g. (Found: C, 67·9; H, 6·0; $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%). This benzophenone gives the same colour reactions as given by 2-hydroxy-4 : 6 : 2′-trimethoxy benzophenone (II *a*). It undergoes demethylation and de-ethylation and ring closure to 1 : 3-dihydroxy xanthone in boiling benzene solution in the presence of anhydrous aluminium chloride.

3 : 4-*Dihydroxy xanthone* (*V*)

(*a*) 2-*Hydroxy*-3 : 4 : 2′-*trimethoxy benzophenone* (*IV*).—This was obtained by the condensation of *o*-methoxy benzoyl chloride (5 c.c.), pyrogallol trimethyl ether (4·2 g.) and anhydrous aluminium chloride (12 g.) in dry ether solution (100 c.c.), the conditions being the same as mentioned earlier. 2-Hydroxy-3 : 4 : 2′-trimethoxy benzophenone crystallised from benzene-petroleum ether mixture as colourless rectangular tablets melting at 110–1° (Found: C, 66·8; H, 5·9; $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%). It dissolves in hot alkali forming an orange yellow solution which deposits a

solid on cooling. It gives a deep red colour with alcoholic ferric chloride solution and forms a deep red solution with concentrated nitric acid which changes yellow on standing. The substance dissolves in concentrated sulphuric acid to an yellow solution exhibiting a bluish green fluorescence.

(*b*) *Demethylation and ring closure.*—The above benzophenone (1·25 g.) was dissolved in dry benzene (50 c.c.), anhydrous aluminium chloride (8 g.) added, the mixture refluxed on a water-bath for 2 hours and the product worked up as in an earlier case. 3 : 4-Dihydroxy xanthone crystallised from dilute alcohol as pale yellow rectangular plates melting at 240–1°.[11] It dissolved in concentrated sulphuric acid to an yellow solution exhibiting a bluish green fluorescence and in aqueous sodium carbonate to give a bright yellow solution. With alcoholic ferric chloride a green colour was obtained.

The diacetate of the xanthone was obtained by boiling with acetic anhydride and freshly fused sodium acetate. It crystallised from alcohol as colourless stout prisms melting at 161–2°.[11]

The dimethyl ether was obtained by methylation of the xanthone with dimethyl sulphate in acetone solution in the presence of anhydrous potassium carbonate. It crystallised from dilute methanol as colourless long needles melting at 156–8°.[12] It dissolved in concentrated sulphuric acid to an yellow solution which developed a bluish green fluorescence on standing.

Gentisin (*VI b*)

(*a*) 2-*Hydroxy*-4 : 6 : 2′ : 5′-*tetramethoxy benzophenone* (*VII*).—2 : 5-Dimethoxy benzoyl chloride (8·3 g.) and phloroglucinol trimethyl ether (6·3 g.), were condensed in the presence of anhydrous aluminium chloride (12 g.) in dry ether solution (100 c.c.). The reaction was carried out as mentioned earlier. The benzophenone crystallised from benzene-petroleum ether mixture as colourless elongated rhombohedral plates melting at 174–5°; yield, 6 g. (Found: C, 64·4; H, 5·9; $C_{17}H_{18}O_6$ requires C, 64·2; H, 5·7%). The substance was slightly soluble in sodium hydroxide in the hot giving an orange yellow solution which deposited a pale yellow solid on cooling. With alcoholic ferric chloride a deep red colour was produced. With concentrated nitric acid a deep red colour changing to deep yellow on standing was obtained. It dissolved in concentrated sulphuric acid to an yellow solution which developed a greenish blue fluorescence on standing.

(*b*) *Demethylation and ring closure to gentisein* (*VI a*).—The benzophenone (1·25 g.) in benzene solution (50 c.c.) was treated with anhydrous aluminium chloride (8 g.) on a boiling water-bath for 2 hours. The rest of the reaction was carried out as mentioned earlier. Gentisein crystallised from dilute alcohol as tiny needles melting at 316–8°.[5] It gave an olive brown colour with

alcoholic ferric chloride, dissolved in sodium hydroxide and sodium carbonate solutions giving an orange yellow colour and in concentrated sulphuric acid to form a deep yellow solution exhibiting a greenish blue fluorescence.

The triacetate of gentisein[13] was obtained by boiling with acetic anhydride and freshly fused sodium acetate. It crystallised from glacial acetic acid in the form of fine silky needles melting at 226°.

(*c*) *Partial methylation of gentisein.*—Gentisein (0·75 g.) was dissolved in dry acetone (50 c.c.), and redistilled dimethyl sulphate (0·3 c.c., 1 mole) and ignited potassium carbonate (1 g.) were then added. The mixture was refluxed on a water-bath for 8 hours, after which time the solution was filtered hot and the potassium salts washed with hot acetone. The solvent was distilled off from the filtrate and the residue dissolved in large volume of ether (200 c.c.). The ether solution was thrice extracted with dilute sodium carbonate solution (10%; 20 c.c. each time) in order to remove any unchanged gentisein. The gentisin in the ether solution was then extracted with sodium hydroxide solution (5%). The alkaline solution was allowed to stand for some time (there was no detectable amount of the sparingly soluble sodium salt of the dimethyl ether) and neutralised with concentrated hydrochloric acid. A gelatinous mass was obtained. It crystallised from alcohol as fine needles melting at 266–7°; yield, 0·5 g. The substance gave an olive green colour with alcoholic ferric chloride and dissolved in concentrated sulphuric acid to an yellow solution which on standing developed a bright green fluorescence. When heated and shaken with sodium amalgam in water it gave a deep green solution which on acidification have a cherry red colour. All these reactions agreed with the reactions recorded for gentisin in the literature. The diacetate of gentisin was obtained by boiling with acetic anhydride and freshly fused sodium acetate. It crystallised from alcohol as thin long woolly needles melting at 196–7°.

(*d*) *Partial demethylation of* 2-*hydroxy*-4: 6: 2′: 5′-*tetramethoxy benzophenone* (*VII*) *to gentisin* (*VI b*).—The above benzophenone (1 g.) was dissolved in acetic anhydride (10 c.c.) and hydriodic acid (10 c.c., 1·7 d.) was then added. The mixture was maintained at a temperature of 110° for a period of half an hour. The free iodine was removed by the addition of sodium bisulphite. The mixture of gentisein and gentisin were separated as in the previous case; yield of gentisein, 0·15 g.; gentisin, 0·1 g.

1: 3: 7-*Trimethoxy xanthone* (*gentisin dimethyl ether*)

Previous investigators did not prepare gentisein trimethyl ether (gentisin dimethyl ether) and record its properties. This has now been done. The

hydroxyl group in 1-position is highly resistant and requires long boiling with excess of dimethyl sulphate to complete the methylation.

Gentisein (0·25 g.) was dissolved in dry acetone (50 c.c.), redistilled dimethyl sulphate (1 c.c.) and ignited potassium carbonate (2 g.) added and the mixture refluxed on a water-bath for a period of 80 hours. The acetone solution was filtered hot and the potassium salts washed with hot acetone. The solvent was distilled off and residue dissolved in ether. The ether solution was washed with dilute alkali in order to remove any partial methyl ether and subsequently with water. The ether was then distilled off and the residue crystallised from dilute methanol when it came out in the form of colourless rectangular plates with a marked tendency to taper at the ends and melted at 171–3°; yield, 0·2 g. (Found: C, 67·6; H, 5·2; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). It dissolved in concentrated sulphuric acid to an yellow solution which developed a greenish blue fluorescence on standing.

Summary

A new synthesis of hydroxy xanthones and their derivatives is described. It employs the Friedel and Craft's reaction for the condensation of an ortho methoxy benzoyl chloride with a fully methylated polyhydric phenol. The resulting benzophenone has an ortho hydroxyl group which in a test case has been shown to belong to the phenol part. By subsequent treatment with aluminium chloride or hydriodic acid demethylation and xanthone ring closure are effected. As examples the synthesis of 1 : 3-dihydroxy xanthone, 3 : 4-dihydroxy xanthone and gentisein is given. The naturally occurring xanthone, gentisin is conveniently obtained by the partial methylation of gentisein or by the partial demethylation and ring closure of 2-hydroxy-4 : 6 : 2′ : 5′-tetramethoxy benzophenone.

References

1. Kostanecki and Nessler .. *Ber.*, 1891, **24**, 3981.
2. Ullmann aud Zloakstoff .. *Ibid.*, 1905, **38**, 2111.
3. Robinson and Nishikawa .. *J. Chem. Soc.*, 1922, **121**, 839.
4. Kostanecki .. *Chem. Zentr.*, 1891, **1**, 587.
5. ——— and Tambor .. *Monatsh.*, 1894, **15**, 1.
6. Shinoda .. *J. Chem. Soc.*, 1927, 1983.
7. Anand and Venkataraman .. *Proc. Ind. Acad. Sci.*, 1947, **25A**, 438.
8. Narasimhachari and Seshadri .. *Ibid.*, 1950, **32A**, 256 and 342.
9. Aghoramurthi *et al.* .. *Ibid.*, 1951, **33A**, 257.
10. Narasimhachari *et al.* .. *Ibid.*, 1952, **36A**, 194.
11. Grabe and Eichengrun .. *Ber.*, 1891, **24**, 967.
12. Ullmann and Denzler .. *Ibid.*, 1906, **39**, 4337.
13. Kostanecki .. *Monatsh.*, 1891, **12**, 209.

SURVEY OF ANTHOXANTHINS—PART II

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In the earlier part[1] were described the methods used for the present survey, and the flavonol composition of (1) Moringa flowers, (2) Neem flowers and (3) Indian podophyllum resin. A number of similar sources known to contain flavonols have further been investigated. These are the flowers of (1) Yellow oleander (*Thevetia neriifolia*), (2) Cambodia cotton (*Gossipium hirsutum*), (3) African marigold (*Tagetes erecta*), (4) *Hibiscus vitifolius* (Tamil: Manjal thuthi), (5) *Hibiscus esculentus* (Hindi: Bhindi) and (6) Yellow roses (*a*) Marechel Neil and (*b*) Lady Hellingden (T.). In most cases the results are interesting and new.

1. *Thevetia neriifolia*

It is an evergreen erect shrub belonging to the family Apocynaceæ, and is well known for its poisonous fruits which contain a cardiac glycoside *thevetin*. Other parts of the plant, such as the leaves and the roots are also considered to be poisonous. The flowers are usually bright yellow and fragrant, but occasionally there are varieties which yield apricot coloured flowers.

Desai and Ahmed[2] were the first to examine the dried flowers and they reported the occurrence of two colouring matters considered to be present as their glycosides. They could not isolate the glycosides, but subjected the crude mixture to hydrolysis with 10% sulphuric acid. The fraction of the aglucone mixture which was insoluble in alcohol was an amorphous brown powder; it did not melt below 360°, and failed to give positive colour tests for the flavone group. Its solution in concentrated sulphuric acid gave a dark green fluorescence. The alcohol-soluble component crystallised from this solvent as yellow needles melting at 260°. It answered the special colour reactions for flavonols and its yellow alkaline solution was decolourised by air. Its solution in concentrated sulphuric acid was yellow with an intense green fluorescence and with alcoholic ferric chloride it gave an intense 'black' colouration. It yielded a tetra-acetyl derivative, contained one methoxyl group and on demethylation gave quercetin. It was therefore believed to be a monomethyl ether of quercetin. As it did not correspond with either rhamnetin or isorhamnetin, it was considered to be a new methyl

ether of quercetin, the 4′-methyl ether. No support either by the degradation or by the synthesis of the compound has so far been provided and the recorded results of analysis for C and H do not agree with the requirements of the proposed monomethyl ether. Later Rao[3] examined these flowers collected and dried at Waltair and reported that they gave only a small yield of a flavonol which was identified as kæmpferol.

For the present survey, the yellow flowers have been collected from different parts of India, Delhi (North), Madras (East Coast) and Cochin (West Coast) and the apricot coloured ones from the Delhi area, and each independently examined. Our results differ markedly from those of earlier workers. In all these cases the pigments are present almost completely as glycosides. Circular chromatography of the aglycones shows the presence of two components having Rf values corresponding to quercetin and kæmpferol. Separation of the glycosides by means of neutral and basic lead salts is found to be inconvenient owing to the presence of large quantities of waxy impurities. But on hydrolysis with mineral acid these impurities are converted into an insoluble condition and could be easily removed, and the aglycone mixture obtained free from them. It could then be conveniently separated by the lead salt method. The component obtained from the neutral lead salt has been identified as quercetin and that from the basic lead salt as kæmpferol, using the methods of mixed chromatography and mixed melting point of the free flavonols and also of the acetates. The yield of the flavonol mixture is roughly 0·15% on the fresh Delhi flowers which works up to 0·2% on the air-dried basis. The flowers do not lose much weight by drying. The proportion of quercetin to kæmpferol is approximately 5 : 1.

2. *Gossipium hirsutum*

Viehoever[4] examined the yellow flowers of the American upland cotton, *G. hirsutum* and obtained from them as the major component quercimeritrin and as the minor component isoquercitrin. The Cambodia cotton widely grown in South India under irrigation belongs to the same species *G. hirsutum* and contains flowers which are only of an ivory colour. Neelakantam and Seshadri[5] examined two samples of these flowers, collected and dried in the seasons of the years 1932 and 1933 respectively. The first collection was found to contain mainly quercimeritrin along with a small quantity of quercetin, whereas the second yielded mainly quercetin along with small quantities of quercimeritrin. No isoquercitrin was detected.

For the present survey a sample of sun-dried flowers has been obtained from Coimbatore. It was rather brittle and had undergone discolouration. Chromatographic analysis of the crude aglucone obtained in the usual way

shows that it consists predominantly of quercetin along with a trace of kæmpferol. The latter could not be isolated by fractionation. When the alcoholic extract of the flowers is concentrated the major portion of the quercimeritrin separates out. The remaining portion is fractionated using neutral lead acetate and basic lead acetate. The neutral lead salt is red and on decomposition yields a glycoside which does not give Pew's reaction and which on hydrolysis yields quercetin. This fraction therefore consists mainly of quercimeritrin, though the presence of quercetin is also possible. The basic lead salt which is yellow and very small in quantity yields on decomposition a glycosidic solution which responds to Pew's reaction and therefore seems to contain a 3-glycoside. On hydrolysis, however, the product is found to be quercetin. It should therefore be concluded that this fraction contains a 3-glycoside of quercetin which is possibly isoquercitrin. It is remarkable that the quercetin derivative like isoquercitrin is not precipitated by neutral lead acetate.[6] The explanation may probably be the existence of some sort of loose combination of the hydroxyl groups in the 3′ and 4′ positions with some other component present in the plant. Such combination is known to take place with sodium borate.[7] Thus the results indicate that the flowers of *G. hirsutum* grown in America and in India have more or less the same composition.

Later a small sample of *G. hirsutum* flowers obtained fresh from the Indian Agricultural Research Institute, New Delhi, towards the end of the last season was examined. It gave a high yield of the pigments (4% on air dried basis) but 50% of it consisted of ether extractable portion (quercetin). Thus it is one of the cases where even fresh flowers contain high quantity of free aglucone.

3. *Tagetes erecta*

These flowers (dried) were examined earlier by Rao and Seshadri[8] and found to contain quercetagetin along with its glucoside quercetagitrin. No other flavonol was reported to be present. The flowers in a fresh condition have now again been examined using the method of circular chromatography. The crude aglucone gives only one ring having Rf value 0·36 which is found to be identical with that given by a synthetic sample of quercetagetin. The total absence of any other component particularly quercetin is quite remarkable. In this respect quercetagetin differs from its isomer gossypetin which is invariably accompanied by more or less quantities of quercetin. This indicates that biogenetically quercetin is more closely related to gossypetin than to quercetagetin. The result is in agreement with expectation from the theory of biogenesis of flavonoids discussed in earlier publications.[9]

4. *Hibiscus vitifolius*

This plant grows wild in the south of India and the flowers are found in abundance during the wet parts of the year. They are sulphur yellow in colour with red eye spots at the base of the petals. Earlier investigations of Rao and Seshadri[10] showed that the fresh flowers form a very good source of the rare 8-glucoside of gossypetin, gossypin. Further it is also a very convenient source for the preparation of gossypetin in large quantities. Smaller amounts of quercetin were also found but since this occurred free it was quite easily separated from the water-soluble glucoside gossypin. In order to see if there could be any other flavonol in this interesting source, a small sample of the fresh flowers has again been examined. They are particularly free from waxy matter and mucilages and hence give clear extracts. The crude aglucone mixture gives only two rings in the circular chromatogram. One of these having Rf value 0·31 is quite bright yellow, gradually turning blue and the other having an Rf value 0·62 is only very weak yellow. These agree with the behaviour of synthetic gossypetin (high concentration) and quercetin (low concentration) respectively. The predominantly major flavonoid component of these flowers is therefore gossypetin (glucoside) with quercetin (free) in very minor quantities as reported by earlier workers.[10]

5. *Hibiscus esculentus*

This plant is grown all over India and is much valued for the green fruits which are used as vegetable. The dried flowers were first examined by Seshadri and Viswanadham[11] who reported the isolation of gossypin in a comparatively poor yield. No quercetin was reported. For the present work fresh flowers have been used. There is considerable difficulty in the extraction owing to the presence of large quantities of mucilages and resins, which also render the isolation of gossypin more difficult. But the aglucone mixture can be obtained satisfactorily pure with less difficulty, the crude yield being 0·3%. Circular chromatography indicates the presence of both gossypetin and quercetin, the former being again the major component, but the ring due to quercetin is brighter than in the case of *H. vitifolius*. Fractionation of the mixture using the acetate method indicates the ratio of the two components to be of the order 9 : 1. The pigments are present completely as their glycosides.

6. *Yellow Roses*

Roses are widely distributed in the world, but true species can be met with only in the wild roses; horticultural roses are the products of considerable intermingling and hence pure species are difficult to obtain. Many of them are known only by their horticultural names.

The red roses are largely cultivated. The colouring matter of these was first examined by Willstatter and Nolan[12] and later by Robinson and Robinson.[13] The former isolated cyanin for the first time from the flowers, and the structure of this has been established to be 3: 5-dimonoside of cyanidin.[14] The latter in the course of their survey of anthocyanins reported that the orange red Polyantha roses like Gloria Mundi and Prince of Orange contain pelargonidin 3: 5-dimonoside (pelargonin) in a pure condition. They also found that in one plant some of the flowers were pink and some orange, the pink containing cyanin and the orange pelargonin.

Though not so numerous as the red roses, yellow roses are also fairly common. Here again, several wild species are reported to exist in different countries. The horticultural varieties are generally known by certain horticultural names, *viz.*, Marechel Neil, Lady Hellingden, McGredy's Sunset, etc. Very little is known about the nature of the colouring matter of these yellow roses. In a programme of study of the flavonoid composition of these flowers, Marechel Neil from Delhi and Bangalore and Lady Hellingden from Delhi have been chosen first. Marechel Neil is a climber which bears bright yellow flowers whereas Lady Hellingden (T.) is a bush type, bearing apricot coloured flowers and having the odour of newly opened tea chest. Both these have been found to be rich in flavonoid pigments, which could be readily obtained pure, because the flowers are markedly free from wax and resin. Results of paper chromatography indicate that in both cases, the pigment consists predominantly of kæmpferol with traces of quercetin. Further, by simple recrystallisation of the flavonol mixture, kæmpferol could be obtained quite pure. It would therefore appear that these flowers could be used as highly convenient sources for the preparation of this flavonol. The pigments seem to occur almost completely as their glycosides.

Experimental

1. *Thevetia neriifolia*

Preliminary investigations.—20 g. each of the various samples of the yellow flowers collected from Madras, Delhi and Cochin, were extracted with hot alcohol and the extracts tested for pigments of the flavone group. An immediate deep red colour with magnesium and hydrochloric acid was given in all cases, thus indicating the presence of flavonols. When the extracts were treated successively with neutral and basic lead acetate, yellow precipitates were thrown out, indicating that the pigments were present most probably as their 3-glycosides. However, with zinc and hydrochloric acid only a green colour instead of a pink colour (Pew's reaction) was developed. This may be due to the interference of extraneous matter which the flowers

are found to contain in plenty. The difficulty persisted even after the glycosides had been precipitated as their neutral and basic lead salts and recovered by decomposition with hydrogen sulphide. But if the recovered glycosidic solutions were extracted repeatedly with ether, the interfering impurities were removed. Then the neutral lead salt fraction gave an immediate test with Pew's reagent, whereas the basic lead salt fraction gave the same only after standing overnight. This may be due to the low concentration of the second fraction or the absence of a 3-glycoside in it. The latter is more probable. The ether soluble portion gave no test with magnesium and hydrochloric acid, and also with alcoholic ferric chloride and therefore contained no flavonols.

Next, the total extracts were hydrolysed in the usual way using 7% sulphuric acid, and the aglycones analysed by chromatography. The results as given in the following table, indicated that in all the different cases, a mixture of two flavonols corresponding to quercetin and kæmpferol was present. The Rf values given by these, however, were slightly higher than the values previously obtained.[1] Since Rf values are liable to vary with conditions[15] a comparison with synthetic samples of quercetin and kæmpferol was done under the same conditions, and their Rf values found to correspond to those obtained for the flower extracts.

TABLE I

(*Temp.* 34°)

	Rf_1	Rf_2
Yellow flowers from—		
1. Madras ..	0·60	0·82
2. Delhi ..	0·62	0·81
3. Cochin ..	0·62	0·82
4. Apricot coloured flowers from Delhi	0·62	0·80
Synthetic quercetin ..	0·62	..
Synthetic kæmpferol ..	..	0·80

Further detailed characterisation of the flavonol mixture was done using both the yellow and the apricot coloured flowers collected locally in Delhi in a fresh condition.

Isolation and separation of the flavonol mixture.—400 g. of the fresh flowers collected from the University gardens were extracted thrice with

hot alcohol, concentrated to a convenient bulk and hydrolysed using 7% sulphuric acid. In the course of hydrolysis considerable amount of a dark solid separated out and the solution was green. The solid was insoluble in ether and gave no test for flavonoids. It was filtered off and the alcohol from the filtrate removed by evaporation. The aqueous solution was then extracted with ether and the ether distilled off. The flavonol mixture was obtained as a yellow residue and separation to the different components was effected through lead salt precipitation. An alcoholic solution of the flavonol aglycones was treated successively with neutral and basic lead acetate and the precipitated lead salts separately decomposed with hydrogen sulphide in alcoholic suspension. The two fractions thus obtained were diluted with excess of water, all the alcohol removed by evaporation and the cold aqueous solutions extracted with ether. On distilling off the solvent, the ether extract gave in each case an almost pure yellow residue. The yield of the residue obtained from the neutral lead salt fraction (I) was approximately 500 mg. and that from the basic lead salt fraction (II) only about 100 mg. When analysed by chromatography, the first one corresponded to quercetin and the second one to kæmpferol. They also answered all the colour reactions characteristic of quercetin and kæmpferol respectively.

The quercetin fraction (I) was treated with alcohol. A small part of it remained undissolved and this was filtered off. A pale yellow crystalline substance, yield 50 mg., was left behind. It melted at 218–20°, was practically insoluble in alcohol, did not give any ferric chloride colour and dissolved with difficulty in concentrated sulphuric acid giving a deep yellow solution showing a faint greenish fluorescence. The substance was, however, readily soluble in cold benzene. Thus it did not seem to belong to the group of flavonoids.

The alcohol-soluble part was crystallised twice from alcohol, yield 300 mg. The acetate was prepared in the usual way by boiling the flavonol (300 mg.) with acetic anhydride (3 c.c.) and pyridine (6 drops) for two hours. It crystallised from ethyl acetate as colourless needles, m.p. 190–91°. The mixed melting point with an authentic sample of quercetin acetate was not depressed (Found: C, 58·1; H, 4·4; $C_{25}H_{20}O_{12}$ requires C, 58·6; H, 4·2%).

The kæmpferol fraction (II) was crystallised first from alcohol and then from boiling toluene; yellow needles, m.p. 273–74°. The mixed melting point with a synthetic sample of kæmpferol was undepressed.

The apricot coloured flowers also yielded almost the same proportions of quercetin and kæmpferol and both were present in the form of their glycosides.

2. *Gossypium hirsutum*

The sun-dried flowers (360 g.) were extracted repeatedly with hot alcohol and the extract concentrated. A small quantity of it was hydrolysed and the crude aglucone chromatographed. Two rings were obtained, the inner deep yellow one, Rf value 0·58, corresponding to quercetin and the outer pale yellow one, Rf value 0·76, corresponding to a trace of kæmpferol.

The rest of the extract was then treated successively with neutral and basic lead acetate. The neutral lead salt fraction was deep brown red and indicated the presence of quercimeritrin. It was deleaded, the alcoholic solution of the glucoside hydrolysed and the aglucone chromatographed, when a single ring corresponding to quercetin was obtained, Rf value 0·55. The yield (1%) was much less than what had been reported earlier, and this may be due to too much sun-drying of the flowers or the lateness of the season of collection.

The basic lead acetate fraction was yellow and the alcoholic solution obtained after decomposing the lead salt gave a positive test for Pew's reaction, indicating the presence of a 3-glycoside. This was hydrolysed using 7% sulphuric acid, and the aglycone analysed by chromatography. A single yellow zone agreeing with quercetin was obtained, Rf value 0·56. The alcoholic solution of the aglycone gave all the colour reactions characteristic of quercetin and a red lead salt with neutral lead acetate. Crude yield of the aglycone 138 mg. (0·03%). The flowers therefore contain quercetin, which is very largely present as quercimeritrin and in a minor portion as a 3-glycoside, probably isoquercitrin.

3. *Hibiscus vitifolius*

The flowers (250) were collected fresh from Madras and extracted with boiling alcohol. The extract was hydrolysed with 7% sulphuric acid. Addition of acid imparted a violet red colour to the solution due to the presence of anthocyanins, which remained in the aqueous solution after ether extraction of the flavonols. The aglucone obtained by evaporation of the ether extract was subjected to circular chromatography when two rings were obtained, an intense yellow inner ring, gradually turning blue, Rf value 0·31, and a faint yellow outer one, Rf value 0·62, agreeing with those of gossypetin and quercetin. No other rings were formed, indicating the absence of other flavonols. The results agreed with the reports of earlier workers[10]; quercetin was present mostly free since it could be extracted with ether before glycoside hydrolysis with mineral acid.

4. *Hibiscus esculentus*

Seshadri and Viswanadham[11] employed the dried flowers for study We have here used fresh flowers and ordinary alcohol (95%) for extraction.

The fresh flowers (200 g.) collected from Madras were extracted thrice repeatedly with hot alcohol, the combined extracts concentrated and hydrolysed. On addition of acid, the extract turned deep red due to the presence of anthocyanins coming from the purple spots at the base of the petals. After extracting the flavonol with ether, these remained in the aqueous solution colouring it deep red. The ether extract was coloured green, due to presence of chlorophyll and on evaporation yielded a yellow residue mixed with plenty of a green oily matter. This was removed by shaking the alcoholic solution with animal charcoal. The yield of the purified pigment was 0·55 g. from 200 g. of fresh flowers.

The crude aglucone on analysis by chromatography gave two rings, having Rf values agreeing with those of gossypetin (0·30) and quercetin (0·60). The inner ring corresponding to gossypetin assumed a blue colour in course of time and was very intense, whereas the outer one (quercetin) was weak indicating that the former pigment formed the major portion of the flavonol mixture.

For separation of quercetin, the aglucone mixture (0·35 g.) was acetylated using acetic anhydride and pyridine, and the acetate fractionated from dry ethyl acetate. Most of the acetate mixture was found to be insoluble in ethyl acetate in the cold. This was filtered off and the melting point determined. It was 226–28°, agreeing very closely with that of gossypetin acetate. The mixed melting point with an authentic sample of gossypetin hexaacetate was undepressed.

The second fraction from the mother liquor sintered at 182° and melted between 185–210°. Obviously it was a mixture of the acetates of gossypetin and quercetin. The last fraction (5 mg.) when crystallised from a mixture of ethyl acetate-petroleum ether, melted at 191–92° and corresponded to quercetin acetate. The mixed melting point with a genuine sample of quercetin penta acetate was also the same. Some more quercetin acetate could be obtained by fractionating the second crop of crystals (m.p. 185–210°). It was deacetylated and the product analysed by circular chromatography when a prominent yellow ring corresponding to quercetin was obtained. The relative proportions of gossypetin and quercetin in *H. esculentus* were found to be approximately 9 : 1. Ether extraction before glycoside hydrolysis yielded no free flavonol and hence both gossypetin and quercetin should be present as their glycosides.

5. *Marechel Neil and Lady Hellingden (T.)*

The petals of the fresh flowers (5 g. each) were first extracted with alcohol, hydrolysed with mineral acid and the aglycone analysed by chromatography. In all cases, two zones were obtained, a very faint inner one corresponding to a trace of quercetin, and a bright yellow outer one corresponding to kæmpferol. Thus kæmpferol was present as the predominantly major component and the trace of quercetin could not be isolated.

TABLE II

(*Temperature* 37°)

Source	Number of zones	Rf_1	Rf_2
Marechel Neil (Delhi) ..	2	0·55	0·78
Marechel Neil (Bangalore) ..	2	0·55	0·80
Lady Hellingden (Delhi) ..	2	0·55	0·75
Synthetic quercetin ..	..	0·56	..
Synthetic kæmpferol ..	..	..	0·76

For further characterisation of the pigments, in the case of Marechel Neil from Delhi, petals of the fresh winter flowers (10 g.) were extracted repeatedly with boiling alcohol and the clear deep yellow extract treated successively with neutral and basic lead acetates. In the neutral fraction, a bulky yellow precipitate was obtained, but only a small quantity of a yellow precipitate was formed in the basic lead salt fraction. These were separately decomposed and the glycosidic solutions hydrolysed by 7% acid in each case; yield neutral lead salt fraction, 0·15 g. or 1·5% and basic lead salt fraction, 0·05 g. or 0·5%. The crude aglycones were then separately analysed by circular chromatography. The neutral fraction gave two rings, a bright yellow one corresponding to kæmpferol and a very faint yellow one corresponding to traces of quercetin, Rf values 0·78 and 0·55 respectively. The presence of kæmpferol as the major component in this fraction was further confirmed by preparing the acetate, which lost water at 118° and melted at 180–82°. The basic fraction on analysis by chromatography gave only a single bright yellow ring, Rf value 0·78, again agreeing with kæmpferol. Its melting point when alone or mixed with synthetic kæmpferol was the same. Mixed chromatography with a synthetic sample of kæmpferol also did not produce any other ring.

Flowers of Marechel Neil from Bangalore, collected in summer (10 g.) were also examined in the same way as above. Here also, the major part of the kæmpferol was found to be precipitated in the neutral lead salt fraction. No quercetin could be isolated from it. The yield was, however, much less than in the case of the fresh winter flowers of Delhi. Yield, neutral fraction, 90 mg. and basic fraction, 10 mg. The pigment was confirmed to be kæmpferol by means of the acetate.

It is remarkable that the major portion of the kæmpferol was precipitated by neutral lead acetate and not by basic lead acetate. Pure kæmpferol when not mixed with quercetin has been found to be precipitated partly by means of neutral lead acetate, but the major portion is precipitated by basic lead acetate. The explanation for this extraordinary behaviour of kæmpferol is not clear and is under investigation. It is possible that this is due to the presence of large quantities of basic inorganic materials in these flowers.

In the case of Lady Hellingden, the petals of the fresh flowers (20 g.) were extracted with alcohol, the extract hydrolysed with acid and the aglycone fractionated through the acetate. All the fractions obtained agreed with kæmpferol acetate in their melting point and no quercetin acetate could be isolated. The yield of kæmpferol in these flowers was exceptionally high 2·5% on the wet flowers which works up to almost 10% on the air-dried matter. The flowers lose weight heavily on drying.

SUMMARY

Fresh flowers are found to be much more satisfactory for getting a true picture of the flavonoid composition than dried ones. The following fresh flowers have now been examined. (1) *T. neriifolia.*—The flowers contain a mixture of quercetin (5 parts) and kæmpferol (1 part) present mainly as their glycosides. (2) *Cambodia cotton flowers.*—These contain almost entirely quercetin most of which is present as quercimeritrin and a very small amount is possibly as isoquercitrin. (3) *T. erecta.*—This contains only quercetagetin in the form of its glycoside. (4) *H. vitifolius.*—These contain mainly gossypetin as the 8-glucoside, gossypin, along with free quercetin in minor quantities. (5) *H. esculentus.*—This is similar to *H. vitifolius* except for the presence of large amount of impurities and seems to contain more of quercetin in the form of glycoside. (6) *Yellow roses*: (*a*) *Marechel Neil and* (*b*) *Lady Hellingden* (*T.*) are good sources of kæmpferol and contain quercetin as a very minor component. These are present as their glycosides.

References

1. Pankajamani and Seshadri .. *Proc. Ind. Acad. Sci.*, 1952, **36 A**, 157.
2. Desai and Ahmed .. *Proc. Nat. Inst. Sci.*, 1939, **5**, 261.
3. Rao .. *D.Sc. Thesis, Andhra University*, 1948.
4. Viehoever .. *J. Agri. Research*, 1918, **13**, 348.
5. Neelakantam and Seshadri .. *Proc. Ind. Acad. Sci.*, 1935, **1**, 887.
6. Perkin and Everest .. *Natural Colouring Matters*, 226 and 228.
7. Shimizu and Ohta .. *J. Pharm. Soc. Japan*, 1951, **71**, 1485 and 1488.
8. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1941, **14 A**, 289.
9. Seshadri and co-workers .. *Ibid.*, 1948, **28 A**, 1; 1949, **30 A**, 333.
10. Rao and Seshadri .. *Ibid.*, 1946, **24 A**, 352.
11. Seshadri and Viswanadham .. *Curr. Sci.*, 1947, **16**, 343.
12. Willstatter and Nolan .. *Ann.*, 1915, **408**, 1.
13. Robinson and Robinson .. *Biochem. J.*, 1934, **28**, 1712.
14. Robinson and Todd .. *J. C. S.*, 1932, 2488.
15. Batesmith and Westall .. *Biochim. Biophys. Acta*, 1950, **4**, 427.

AMPHIBOLITE-GRANULITE FACIES CHARNOCKITES

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Introduction

The Problem

The problem of the origin of the charnockites has been a much disputed one. Holland considered that the charnockites formed a magmatic series varying from acid to ultrabasic types and unified the series into a petrographic province. Vredenburg held the view that the charnockites were metamorphosed Dharwars. A detailed study of the type area affords enough evidence to consider that the rocks constitute a high grade metamorphic suite approaching the granulite facies. There have been oscillations in the P.T. conditions as shown by the prograde and retrograde mineral reactions. The type area itself shows rock-types which have resulted by allo-chemical metamorphism. The same theory may possibly hold good for the charnockites of batholithic dimensions, particularly in the light of modern ideas that the pegmatites and cross-cutting dykes, can be formed by metasomatic replacement.

Geological Setting

Cherimalai (sheet 66 D/15; Lat. 80° 10′ 55″: Long. 12° 57′ 25″) and Parvattai malai to its west, situated barely two miles to the south-east of the Mosque Hill Pallavaram, the type area for charnockites affords a very interesting study. The prominent rock-type not hitherto observed is a band of garnetiferous-diopside-granulite with a thickness varying from a few feet to a maximum of sixty feet making up nearly one-third of the southern flank of the hill. This rock occurs interbanded with the leptynites and gradually disappears into the norites. Detailed mapping (Fig. 1) resolves the charnockites in the area into noritic-boulders, and bands of varying sizes of biotite-norite, hornblende-garnet-spinel rocks and garnetiferous-diopside-granulite already referred to. This last member shows thin bands of scapolite-calc-granulite which formed the subject of a paper (Muthuswami, 1951). The calc-scapolite bands of thickness varying from half to one inch have also been observed in the Mosque Hill Pallavaram, described in Holland's Memoir (1900). There are stringers of norite in the garnetiferous-diopside-granulite; some of these spread out into irregular patches. All gradations of rock-types with hypersthene to those without hypersthene are

fairly common. There is no definite cross-cutting relationship of the norite to consider it as intrusive; neither are there clear evidences of recrystallization of minerals at the contacts of norite bands.

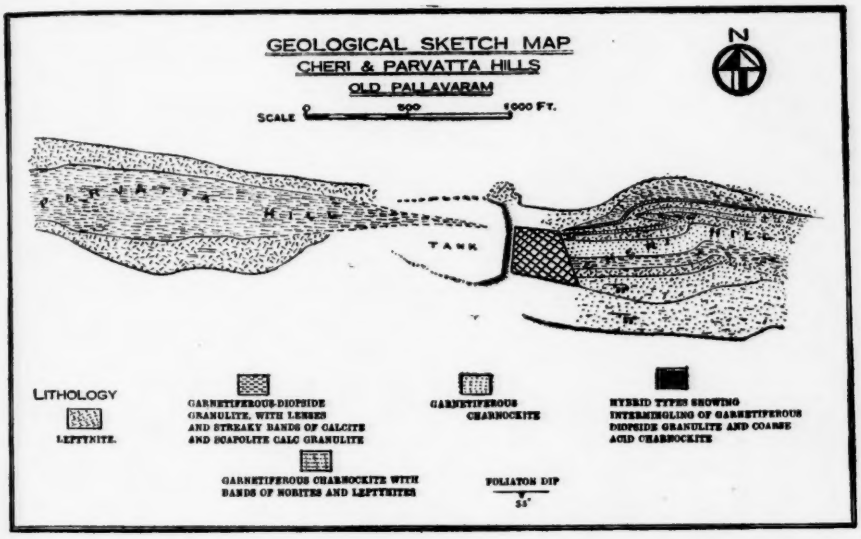

FIG. 1

There are indications of minor pitching folds of bands of basic granulite and leptynite on the northern flank towards the east. One could observe long-drawn-out bands of blue quartz. The lineation is 35 to 40 degrees to east-south-east. The basic rock-types include:

(i) Garnetiferous-diopside-granulite.
(ii) Hornblende-norite.
(iii) Biotite-norite.
(iv) Garnet-hornblende-spinel-rock.
(v) Norite.

MINERALOGY

General Statement

The most important minerals are plagioclase, pyroxene, hornblende, garnet, biotite, spinel, apatite and ores. Calcite occurs associated with scapolite and sphene, in scapolite-calc-granulite. It also occurs sparingly in some of the associated rock-types. Quartz is present in subordinate quantities.

Methods of Study

Indices of Refraction.—Refractive indices were obtained by immersion methods using white light. The R.I. of liquids were simultaneously determined by Abbé Refractometer or Leitz-Jelley Micro-Refractometer. Estimated possible errors are ± ·002. Optic axial angles and the twin laws of the plagioclases were found on the five-axis universal stage. The anorthitic content was estimated not only from the 2 V values but also from sections normal to the composition plane (010) and normal to the ă axis. The specific gravity of garnet was determined by the pyknometer.

Micro-Petrography

Garnetiferous-diopside-granulite

Plagioclase.—The twins are mostly albite-normal with pericline striations; the twin bands are sometimes wedge-shaped and extinction undulose. The mean R.I. is 1·559; $2V_z$ is 80°. The composition is $Ab_{50}An_{50}$. Subcalcic plagioclases occur as inclusions in the calcic ones and sometimes the former cut across the twin bands of the latter. Such grains are mostly irregular in outline with diopsidic inclusions. Small anhedra of plagioclase also occur as inclusions in the pyroxene grains that show lamellar growths of diopside and hypersthene. Blebs of released quartz are fairly common.

Pyroxenes.—Both rhombic and monoclinic varieties are present. There is much variation in the 2 V and R.I. values; however the orthopyroxene of the intergrowth is eulite and the monoclinic variety is augite or salite. The minerals that have intergrown have the following characteristics:—

		Intergrowth	
		Orthorhombic pyroxene	Monoclinic pyroxene
Pleochroism	X	Pink	Green
	Y	Yellow	Green with a tinge of brown
	Z	Green	Green
Ref. Indices	*nx*	1·701	..
	ny	..	1·704
Birefringence		..	·028
	2 V	63°	59°
Sign		Negative	Positive
Parting		‖ to (001)	‖ to (001)
Composition		Eulite (of 70 en 30)	20% Fe atoms in 50% Ca + Mg + Fe atoms augite or salite
		(Poldervaart, 1947)	(Hess, 1949)

The intergrowth produces a blurred colour effect on rotating the stage when the nicols are not crossed, an effect which is clearly seen in thick sections where the pleochroism of hypersthene dominates. The intergrowth is interrupted by salite veins and by hypidiomorphic grains (Micro-photo 1). The crystallographic (Hess, 1940) and optical orientations are given in Fig. 2.

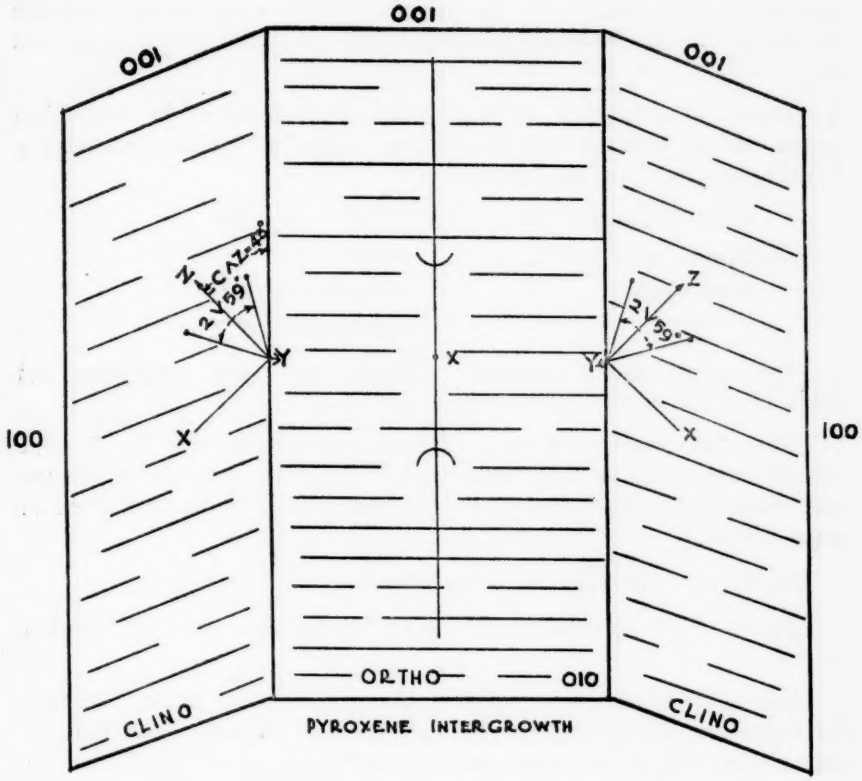

FIG. 2

The orthopyroxene crystallographic orientation is after Hess (1940); (100) is the junction plane of the two minerals; the X of hypersthene and Y of salite coincide; (001) salite lamellæ, make an angle of 20 degrees with (001) of the orthopyroxene.

Some hypersthene grains give inclined extinction up to 20 degrees. Hess (1938) explains this, as due to a composite effect brought about by the lamellæ dipping at low angles to the plane of the section. Under crossed nicols such sections simulate polysynthetic twinning. Sections parallel

to (100) of the hypersthene reveal the sharp lamellæ of salite in the extinction position of the orthopyroxene. Occasionally the herring-bone structure (Micro-photo 2) associated with clinopyroxene is also observed in combination with lamellar structure. Inclusions of plagioclase are common in the lamellar intergrowths.

Hypersthene is also observed as a reaction mineral at the junction of ore and salite (Micro-photo 3). The rhombic pyroxene completely surrounds the ore and merges insensibly into salite. This is feebly pleochroic and has $2V_x = 65°$.

Garnet.—The mineral is mostly anhedral, embayed by plagioclase giving rise to irregular dented outlines. Euhedral crystals indicating a centrifugal growth are also present.

Refractive index	1·794	
Specific gravity	4·06	
Composition	Grossularite	33%
	Almandite	67%

The mineral shows vermicular inclusions of quartz, plagioclase and relicts of pyroxene intergrowths (Micro-photo 4).

Garnet is developed fringing (1) iron ores (Micro-photo 5), (2) salite and (3) intergrowths of hypersthene and salites when these are at contacts with plagioclase (Micro-photo 6). The reaction equations are given in pages 739–40.

Hornblende.—The mineral is sparingly present.

Quartz.—This also occurs in minor quantities mostly as released mineral.

Texture.—The texture is granulitic; the crystalloblastic fabric, the bent and wedge-shaped twinning lamellæ, the undulose extinction, the veins of salite cutting across the intergrowths are evidences of recrystallization in a solid environment.

The chemical analysis of a representative specimen is recorded in Table I with some geochemical data.

Hornblende-norite.—The micro-characters of the important constituents plagioclase, hypersthene and diopside are in all respects similar to those already described.

TABLE I

Garnetiferous-diopside-granulite, Cheri Hill, Pallavaram

Constituents	Weight percentages	Niggli values	Basis molecules	Katanorm	CIPW norm.
SiO_2 ..	47·66	..	..	..	..
Al_2O_3 ..	19·51	si −107·40	Kp − 0·9	Q− 0·54	Q − 4·74
Fe_2O_3 ..	3·50	al − 25·86	Ne − 3·8	Or− 1·50	Or − 1·11
FeO ..	9·36	fm− 37·95	Cal −30·5	Ab− 6·33	Ab − 5·76
MnO ..	..	c − 34·35	Cs − 6·5	An−54·16	An −49·48
MgO ..	4·30	alk − 1·84	Fs − 3·8	Wo− 7·47	Di { Wo− 8·82
					Di { En − 4·00
CaO ..	14·18	ti − 1·49	Fa −11·1	En−12·13	Di { Fs − 4·75
Na_2O ..	0·66	k − 0·19	Fo − 9·1	Hy−12·27	Hy { En − 6·80
K_2O ..	0·25	mg− 0·38	Ru − 0·6	Tn− 1·80	Hy { Fs − 8·05
TiO_2 ..	0·87	..	Q −33·7	Mt− 3·80	Mt − 5·10
P_2O_5 ..	..	..	..	..	Il − 1·67
H_2O ..	+0·16	..	..	..	Water− 0·16
	100·45			100·00	100·44

Analysis : Department of Geology, Presidency College, Madras.

Hornblende is greenish brown and is present in appreciable quantities. Its characters are:—

$Z > Y > X$

nx	..	..	1·672
ny	..	..	1·679
nz	..	..	1·693
$2V_x$	..	..	72°
$C \wedge Z$	..	..	− 12°

Biotite is observed and calcite is of rare occurrence.

Washington's (1916) analyses of the rock is reproduced with geochemical data in Table II.

Biotite-norite.—Plagioclase is of the andesine variety; the rhombic pyroxene is enstatite; diopside is practically colourless. Biotite is formed secondarily along the cleavage cracks and sometimes shoots itself into the cleavages of felspars (Micro-photo 7). The mineral is deeply pleochroic from brown to colourless and contains numerous pleochroic haloes. Hornblende is observed only in small quantities. Apatite and iron ores are fairly common. The chemical analysis and the calculated data are given in Table III.

TABLE II

Hornblende-Norite, St. Thomas Mount, Madras

Constituents	Weight percentages	Niggli values	Basis molecules	Katanorm	CIPW norm
SiO_2 ..	50·04	si −118·00	Kp − 3·43	Or − 5·72	Or − 5·00
Al_2O_3 ..	11·65	al − 16·27	Ne −17·23	Ab −28·72	Ab −26·20
Fe_2O_3 ..	2·63	fm − 55·30	Cal − 9·49	An −15·81	An −15·29
FeO ..	15·76	c − 19·95	Cs − 7·40	Wo − 7·10	Di { Wo − 9·40, En − 3·54, Fs − 6·07
MnO ..	..	alk − 8·48	Fs − 2·83	En −10·21	Hy { En − 7·74, Fs −13·20
MgO ..	5·58	ti − 3·40	Fa −18·72	Hy −14·54	
CaO ..	7·89	k − 0·17	Fo −12·13	Fo − 4·48	Ol { Fo − 1·82, Fa − 3·36
Na_2O ..	3·08	mg − 0·36	Ru − 1·38	Fa − 6·40	
K_2O ..	0·89	..	Q −27·33	Tn − 4·14	Mt − 3·82
TiO_2 ..	1·93	..	..	Mt − 2·83	Il − 3·65
P_2O_5 ..	0·20	..	..	..	Ap − 0·50
H_3O^+ ..	0·19	..	..	..	
	99·84		99·94	99·95	99·59

Analyst: Washington.

TABLE III

Biotite Norite, Pallavaram

Constituents	Weight percentages	Niggli values	Basis molecules	Katanorm	CIPW norm
SiO_2 ..	49·76	si −128·10	Kp − 13·07	Or − 21·78	Or −20·90
Al_2O_3 ..	18·27	al − 27·67	Ne − 16·51	Ab − 25·00	Ab −21·36
Fe_2O_3 ..	2·68	fm − 37·71	Cal − 15·42	Ne − 1·51	Ne − 2·18
FeO ..	9·35	c − 21·33	Cs − 4·73	An − 25·70	An −25·76
MnO ..	..	alk − 13·30	Fs − 2·92	Wo − 6·30	Di { Wo − 5·29, En − 2·03, Fs − 3·33
MgO ..	3·21	ti − 2·16	Fa − 11·18	Fa − 9·72	Ol { Fo − 4·20, Fa − 7·65
CaO ..	7·73	k − 0·40	Fo − 6·88	Fo − 6·88	
Na_2O ..	3·02	mg − 0·30	Ru − 0·23	Ru − 0·23	{ Mt − 3·87, Il − 1·98
K_2O ..	3·56	..	Q − 29·09	Mt − 2·92	Water − 1·19
H_2O+ ..	0·12	..	..	..	..
H_2O- ..	1·07	..	..	..	..
	99·77		100·03	100·04	99·74

Analysis : Department of Geology, Presidency College, Madras.

Garnet-hornblende-spinel-rock.—Plagioclase is $Ab_{35}An_{65}$. Garnet hornblende and spinel are the conspicuous minerals. Hornblende is formed along the cracks in garnets. The garnet contains inclusions of hornblende,

spinel and plagioclase derived from the disintegration of the mineral (Microphoto 8). Hornblende has the following characters:—

Z > Y > X		
X	.. .. ..	Yellow
Y	.. .. ..	Pale Yellow
Z	.. .. ..	Brown
$2V_x$	.. .. ..	71°

Biotite is clearly secondary after hornblende; pleochroic haloes are rare.

The chemical composition and the chemical values are given in Table IV.

TABLE IV

Garnet-hornblende-spinel rock, Cheri Hill

Constituents	Weight percentages	Niggli values	Basis molecules	Katanorm	CIPW norm
SiO_2 ..	40·84	si – 82·94	kp – 1·70	Or – 3·97	Or – 2·78
Al_2O_3 ..	27·21	al – 32·52	Ne – 7·00	Ab – 4·42	Ab – 5·40
Fe_2O_3 ..	2·16	fm – 37·64	Cal – 36·40	An – 60·66	An – 60·88
FeO ..	7·87	c – 26·67	Sp – 3·70	Ne – 4·15	Ne – 3·01
MnO ..	..	alk – 3·17	Fo – 12·40	Sp – 3·70	C – 2·24
MgO ..	6·83	ti – 0·97	Fa – 9·10	Fo – 12·40	Or { Fo – 11·97
CaO ..	12·25	k – 0·19	Fs – 2·40	Fa – 7·90	Or { Fa – 8·98
Na_2O ..	1·27	mg – 0·55	Ru – 0·40	Ru – 0·40	Mt – 3·25
K_2O ..	0·52	..	Q – 26·90	Mt – 2·40	Il – 1·22
TiO ..	0·60	..	..	..	..
H_2O^+ ..	0·97	..	..	..	..
H_2O ..	0·08	..	..	..	..
	100·60		100·00	100·00	99·73

Mode

Plagioclase	.. 33·0
Garnet	.. 35·0
Hornblende	.. 28·0
Spinel	.. 2·0
Quartz	.. 1·0

Analysis : Department of Geology, Presidency College, Madras.

Norite.—Plagioclase ($Ab_{52}An_{48}$), hypersthene and diopside are present. But the intergrowth of the ortho and clinopyroxenes so distinguishing a feature of the latter is completely absent. Further garnet is also absent. Hornblende is of rare occurrence and quartz when present is a released mineral. The texture is granulitic.

The chemical analysis of norite with the chemical data is recorded in Table V.

TABLE V

Norite, Cheri Hill

Constituents	Weight percentages	Niggli values	Basis molecules	Katanorm	CIPW norm
SiO_2 ..	50·87	si −122·36	Kp − 2·04	Q − 4·34	Q − 5·10
Al_2O_3 ..	18·88	al − 26·70	Ne − 9·19	Or − 3·40	Or − 2·78
Fe_2O_3 ..	2·83	fm − 42·86	Cal − 25·86	Ab − 15·32	Ab −14·15
FeO ..	8·99	c − 25·68	Cs − 2·21	An − 43·10	An −42·53
MnO ..	..	alk − 4·76	Fs − 3·06	Wo − 2·49	Di { Wo − 3·02
					Di { En − 1·50
MgO ..	5·43	ti − 1·15	Fa − 10·65	En − 15·44	Di { Fs − 1·45
CaO ..	9·98	k − 0·18	Fo − 11·58	Hy − 12·16	Hy { En −12·10
					Hy { Fs −12·14
Na_2O ..	1·72	mg − 0·46	Ru − 0·23	Tn − 0·69	Mt − 4·18
K_2O ..	0·56	..	Q − 35·18	Mt − 3·06	Il − 0·61
TiO_2 ..	0·36	..	..	..	..
H_2O ..	0·06	..	..	..	
	99·68		100·00	100·00	99·56

Analysis : Department of Geology, Presidency College, Madras.

There are also types with plagioclase, garnet, diopside without hypersthene and with small quantities of brown hornblende, calcite, biotite and apatite.

A study of Niggli data shows that:—

(i) there is a close similarity in the Niggli values of the garnetiferous diopside-granulite and norite that they may be considered to have a genetic relationship;

(ii) that the hornblendic and biotite-norites have had possibly differences in original chemical composition;

(iii) that in these, the group of basis molecules are the same since $K + Na < Al$, and $K + Na + 2\,Ca > Al$; and

(iv) that the garnet-spinel-rock shows a clear difference in the bulk composition, as spinel is present in the katanorm.

METAMORPHIC FACIES

The equilibrium assemblages of the three associated phases with quartz as a fourth one are shown in Fig. 3. Hornblende and biotite are additional ones. The former makes its appearance in calcic-rich rocks while the latter in potash-rich rocks.

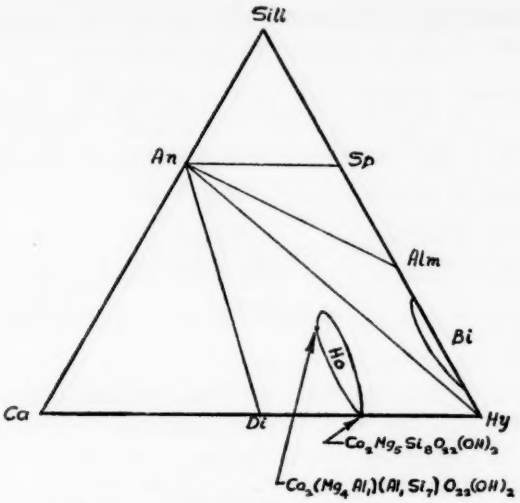

FIG. 3. ACF Diagram—on the basis of atoms Al, Ca and Mg

Rocks with the association

(*a*) diopside-plagioclase-hypersthene;

(*b*) almandite-plagioclase-hypersthene, conform to the usual paragenesis. Diopside and almandite do not occur together in stable equilibrium in the granulite facies. Such an association in the garnetiferous-diopside-granulite should be considered as a state of chemical dis-equilibrium. Exceptional occurrences of this kind have also been reported from Adelie Land (Stillwell, 1918), Uganda (Groves, 1935) and Sweden (Quensel, 1951).

The garnetiferous-diopside-granulite is a passage rock between these two facies, as revealed by its paragenesis-diopside, garnet, hypersthene and plagioclase.

The reactions may be indicated by the following equations:—

$$15\,[CaO\,(Mg, Fe)\,O\cdot 2\,SiO_2] + \begin{bmatrix} 6\,(CaO\cdot Al_2O_3\cdot 2\,SiO_2) \\ 3\,(Na_2O\cdot Al_2O_3\cdot 6\,SiO_2) \end{bmatrix} + 4\,Al_2O_3 \rightarrow$$

Diopside + Calcic plagioclase + Alumina →

$$\begin{bmatrix} 4\,(3\,CaO\cdot Al_2O_3\cdot 3\,SiO_2) \\ 3\,(3Mg, Fe)O\cdot Al_2O_3\cdot 3\,SiO_2 \end{bmatrix} + 6\,[(Mg, Fe)\,O\cdot SiO_2] + \begin{bmatrix} 3\,(CaO\cdot Al_2O_3\cdot 2\,SiO_2) \\ 3\,(Na_2O\cdot Al_2O_3\cdot 6\,SiO_2) \end{bmatrix}$$

Garnet + Hypersthene + Sub-calcic plagioclase

$+ 6\,CaO + 9\,SiO_2$

+ lime + quartz (1)

If the recrystallization process is not complete the paragenesis diopside, garnet, hypersthene and plagioclase would result.

The occurrence of hornblende in a water-deficient system such as the granulite facies is an interesting feature. The small quantities of hornblende in association with garnet and blebs of quartz is explained thus:

$$7\,(Mg, Fe)\,SiO_3 + Ca_2Na \cdot Al_5Si_7O_{24} + H_2O \rightarrow$$
Hypersthene + Plagioclase + Water
$$Ca_2Na\,(Mg, Fe)_4Al_3Si_6O_{22}\,(OH)_2 + (Mg, Fe)_3Al_2Si_3O_{12} + 5\,SiO_2$$
Hornblende + Garnet + Quartz (2)

Also,

$$NaCaAl_3Si_5O_{16} + Ca\,(Mg, Fe)\,Si_2O_6 + 3\,(Mg, Fe)\,SiO_3 + H_2O \rightarrow$$
Plagioclase + Diopside + Hypersthene + Water
$$NaCa_2\,(Mg, Fe)_4Al_3Si_6O_{22}\,(OH)_2 + 4\,SiO_2$$
Hornblende + Quartz (3)

In equations (2) and (3) water is a component in the reactions. In the practically anhydrous system such as the granulite facies " water itself constitutes an additional component permitting crystallization of an additional hydrous phase, namely hornblende, in appropriate mineral assemblages " (Turner, 1949).

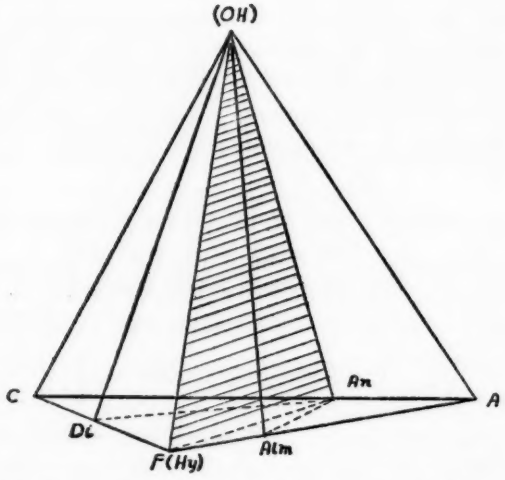

FIG. 4. Tetrahedral projection-ACF, with H_2O at the apex

In the tetrahedral projection (Fig. 4) using the ACF triangle as the base, and with water at the apex as the fourth component the following paragenesis are admissible:—

(*a*) Diopside-plagioclase-hypersthene-hornblende.

(*b*) Almandite-plagioclase-hypersthene-hornblende.

It is clear that almandite and diopside that are not stable together are separated by the "wall" hypersthene-plagioclase-hornblende. But due to chemical disequilibrium, as already said, diopside and garnet occur in the rock under description.

The presence of biotite may be explained in a similar way.

The synantectic formation of garnet at contacts of plagioclase with hypersthene or iron ore, the inclusion of released quartz in diopside, relict lamellar intergrowths of diopside-hypersthene in garnet, the anomalous double refraction of garnet in the intimately associated lime-rich granulite are evidences to show that there have been incipient adjustment of the rock-mass to conditions of slow cooling and release of load. The retrograde metamorphism, it may be inferred, has just reached a stage transitional between the typical granulite facies as exemplified by the norite and the almandine-diopside-hornblende subfacies of the amphibolite facies.

It is interesting as shown below that the scapolite-calc-granulite is also isofacial with the garnetiferous-diopside-granulite. Where the original rocks have been calcareous, plagioclase, pyroxene and calcite have been developed with quartz. The presence of calcite and quartz in the calc-granulite suggests that the prevailing pressures should have been high enough to permit the formation of calcite or dolomite and inhibit the formation of wollastonite. The rock cannot be classified under the granulite facies (plutonic metamorphism without stress) as sphene which is invariably absent in the granulite facies, is present in the rock. So it has to find a place high up in the amphibolite facies, namely the diopside-almandine-amphibole subfacies, which corresponds to the sillimanite zone of regional metamorphism.

A general retrograde metamorphic effect is inferred from the presence of the lamellar intergrowths of salite and hypersthene. These intergrowths do not seem to be contemporaneous; the two parts may be considered as exsolved products of a single phase on cooling. An alternative explanation also suggests itself. These intergrowths are combined occasionally with the herring-bone structure which is characteristic of clinopyroxene. The factors favourable for the solution of CaO in the clinopyroxenes are the availability of lime not only in the calcic plagioclase (Equation 1) but also

in the closely associated bands of calc-granulite. Calcium has greater mobility under depth conditions and its solubility increases in the presence of CO_2. With fall of temperature and escape of CO_2 that follows the retrograde process, favourable conditions set in for CaO, which has a high velocity of diffusion, to get into the weak spots of the lime-free clinopyroxenic constituents and give rise to the diopsidic lamellæ; the hypersthene lamellæ are probably due to inversion.

It is also possible that the presence of fluorine and chlorine, as evidenced by the scapolitization of the plagioclases and occurrence of apatite, may disturb the bonding of the mineral phases and aid the intergrowth formations.

The two other basic rock-types hornblende-norite and hornblende-garnet-spinel-rock are also practically isofacial with the other types. They are unsaturated and the CIPW norm and Niggli katanorm do not show normative quartz. As under such conditions, hornblende can be stable in the granulite facies, the two rocks can be considered to belong to the granulite facies. Ramberg (1949) points out that hornblende can be present abundantly in the basic members of the charnockite series, provided there is an increase of anorthite in the plagioclase molecule. The reaction is given by equation

$$\underset{\text{Hypersthene}}{7\,(Mg, Fe)\,SiO_3} + \underset{\text{Plagioclase}}{NaCa_2Al_5Si_7O_{24}} \rightarrow \underset{\text{Hornblende}}{NaCa_2\,(Mg, Fe)_4Al_3Si_6O_{22}\,(OH)_2} + \underset{\text{Garnet}}{(M, Fe)_3Al_2Si_3O_{12}} + \underset{\text{Quartz}}{5\,SiO_2} \quad (4)$$

The anorthitic content of 65 per cent. is sufficiently high to bring about such a displacement and the assemblage garnet, hornblende and spinel as shown below:—

$$\underset{\text{Hypersthene}}{12\,(Mg, Fe)\,SiO_3} + \underset{\text{Plagioclase}}{3\,NaCa_2Al_5Si_7O_{24}} + \underset{\text{Water}}{2\,H_2O} \rightarrow \underset{\text{Hornblende}}{2\,NaCa_2\,(Mg, Fe)_4Al_3Si_6O_{22}\,(OH)_2} + \underset{\text{Garnet}}{(Mg, Fe)_3Al_2Si_3O_{12}} + \underset{\text{Spinel}}{(Mg, Fe)\,O\cdot Al_2O_3} + \underset{\text{Plagioclase}}{NaCa_2Al_5Si_7O_{24}} + \underset{\text{Quartz}}{11\,SiO_2} \quad (5)$$

The formation of biotite in the hornblende-norite and biotite-norite is dependent on the proportion of $K_2O/(Mg, Fe)\,O$ and Al_2O_3. The potash

content in biotite-norite is 3·56 per cent., much higher than that in hornblende-norite which is 0·89 per cent.

Thus the rock-types show the paragenesis of the granulite facies with however a general tendency to approach the almandine-diopside-hornblende subfacies of the amphibolite facies.

The granulitic facies exemplifies the highest grade in regional metamorphism. The norite belongs to this grade. The other rock-types show a retrograde metamorphic character. It is not likely that the chemical composition of the premetasomatic complex was so uniform in character that all the types could have been derived entirely by diffusion from norite in a regional metamorphic environment.

However the microscopic and petrochemical evidences tend to indicate that the garnetiferous-diopside-granulite has been essentially derived by metasomatic diffusion in the said environment, the necessary heat for metamorphism being obviously obtained from the emanations that carry the material.

A quantitative idea of the extent of the diffusion effect has been rendered possible by Barth's Standard Cell Method. The underlying principles of this method are:

(1) That metasomatic replacement of rock takes place under isovolumetric conditions.

(2) In the majority of rocks 94 per cent. by volume is made up of oxygen and 6 per cent. by cations (silicon and metals).

(3) Since metasomatism takes place volume for volume, under the conditions that 94 per cent. of any rock is made of oxygen ions, it follows that the number of oxygen ions in all rocks is about the same.

(4) It would therefore be appropriate in metamorphic studies, where there are evidences of say, a rock *A* getting metasomatized to *B*, to determine the inflow and outflow of the stream of cations in terms of oxygen ion standard. Such a quantitative study with reference to a suite of isofacial rocks would give a clear picture of the fundamental aspects of the problem. It is obvious that one of the rock-types should be considered the mother rock, for purposes of tracing the descent of the other associated types.

(5) The constitution of most rocks is such that for 160 oxygen ions there are approximately 100 cations. Hence the number of cations linked up with 160 oxygen ions, gives directly the approximate percentage of the constituent cations. It would therefore be appropriate to take 160 oxygen

ions, *i.e.*, 320 valences as a morphological unit of a rock in determining the percentage of cations for that rock. This morphological unit is called the 'Standard Cell'. Its chemical content defines the chemical formula of the rock.

(6) Since 320 valences bind the cations, the number of valences must clearly balance in the exchange of cations in metasomatic diffusion.

Table VI gives the mode of calculation of the Standard Cell for the mother rock norite and its chemical formula.

TABLE VI

Cheri Hill-Norite

1	2	3	4	5	6	7	8
Constituents	Weight percentage	Molecular weight	Mol. prop. ×1,000	Cations prop. ×1,000	$\frac{(5)\times 100}{1761\cdot5=(5)\times\cdot0567}$	Number of oxygen ions for 100 cations	No. of cations in the standard cell $\frac{(6)\times 160}{161\cdot545=(6)\times\cdot99040}$
SiO_2 ..	50·87	60·06	847·0	847·000	48·024	96·048	47·563
Al_2O_3 ..	18·88	101·97	185·1	370·200	21·090	31·635	20·887
Fe_2O_3 ..	2·83	160·00	17·69	35·380	2·006	3·009	1·987
FeO ..	8·99	72·00	124·0	124·000	7·030	7·030	6·693
MgO ..	5·43	40·32	134·7	134·700	7·637	7·637	7·564
CaO ..	9·98	56·00	178·2	178·200	10·103	10·103	10·006
Na_2O ..	1·72	62·00	27·74	55·580	3·151	1·575	3·121
K_2O ..	0·56	94·00	5·958	11·916	0·699	0·349	0·692
TiO_2 ..	0·36	80·00	4·500	4·500	0·255	0·127	0·252
				1,761·476	99·995	157·513	99·035
H_2O ..	0·64	18·00	35·550	71·100	4·032	4·032	(3·993)
	100·26	..		..		161·545	

$K_{0\cdot09}Na_{3\cdot12}Ca_{10\cdot01}Mg_{7\cdot56}Fe_{8\cdot95}Al_{20\cdot89}Si_{47\cdot56}Ti_{0\cdot28}[O_{152}(OH)_8]_{160}$.

In a similar way the chemical formula of the garnetiferous-diopside-granulite is found to be:—

$K_{0\cdot30}Na_{1\cdot32}Ca_{14\cdot69}Mg_{6\cdot18}Fe_{10\cdot02}Al_{22\cdot18}Ti_{0\cdot60}Si_{46\cdot00}[O_{158\cdot84}(OH)_{1\cdot16}]_{160}$

The transfer of cations in the formation of garnetiferous diopside-granulite from norite is given in Table VII.

It would be reasonable to expect variations in the composition in the metasomatized rocks also due to the physical factors of cohesion, cleavage, lattice structure of the minerals. Further the energy of activation and the mobility of the activating medium may vary from place to place. This perhaps explains why the valences cannot be balanced to the exactitude demanded by theory, from the chemical data of average specimens.

TABLE VII

Norite passes into granetiferous-diopside-granulite by

Addition of cations	Valences	Removal of cations	Valences
Fe 1·07	7·03	K 0·39	0·39
Al 1·29	3·87	Na 1·80	1·80
Ca 4·68	9·36	Mg 1·38	2·76
Ti 0·35	1·40	Si 1·56	6·24
			H in (OH) 6·84
7·39	21·66	5·13	18·03

CONCLUSION

Stillwell (1911) after a critical examination of Holland's (1900) views considered that the characters form and structure, dykes and apophyses, as well as the chemical and mineralogical evidences can be explained on the basis of recrystallization under katazone conditions equivalent to the granulite facies. Fermor (1936) has considered the possibility of hypersthene of charnockites not being magmatic but as due to " a signature tune of common high grade metamorphism effected at unusual depths below the surface ". Ghosh (1941) has also shown that the breakdown of hypersthene into diopside and hornblende or to biotite is effected under the influence of alkaline fluids. B. Rama Rao (1945) considers that " the combined effects of a repeated series of alterations under different periods of metamorphism of a composite series of rock-formations of *different ages*, have given rise to a series of hypersthene-granulites of very variable composition ". He is a supporter, though with reserve of Vredenburg's (1918) view that the charnockites represent a series of the igneous members of the Dharwars.

This type area near Madras—a classic ground for the study of charnockites, affords enough data for the metamorphic origin of the suite of rocks. The norites of the area might have resulted from calc-alkaline-shale in the deep-seated folds of a precambrian orogenic phase, where depth and temperature combined to expel the water—a feature of the granulite facies.

SUMMARY

The Cheri Hill in the Madras type area of charnockites, shows on careful mapping the folding of bands of leptynite and basic charnockites. The mineralogy of the basic types gives striking evidences of the metamorphic origin of charnockites. The rocks have been subjected to some little retro-

grade metamorphism and are ascribed to the almandine-diopside-hornblende subfacies of the amphibolite facies. A quantitative idea of the influx and efflux of ions is worked out on the lines of Barth, in the process of replacement of the norite to the associated garnetiferous-diopside-granulite.

ACKNOWLEDGEMENT

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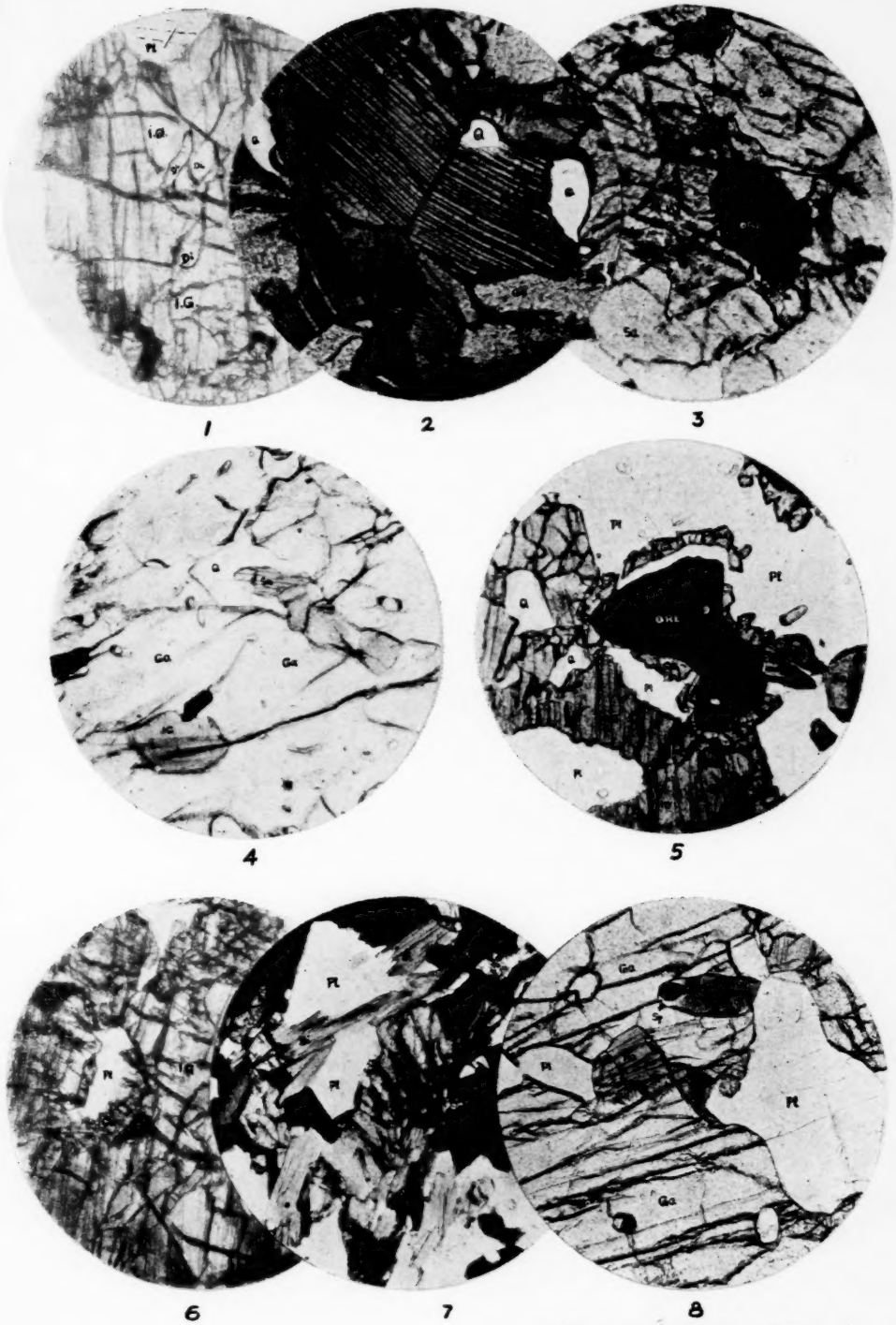
REFERENCES

Barth, T. F. W. .. *Theoretical Petrology*, John Wiley, 1951.
Emmons, R. C. .. *Mem. Geol. Soc. America*, **8**.
Fermor, L. L. .. *Mem. Geol. Surv, India*, 1936, **70**, 42.
Ghosh, P. K. .. *Rec. Geol. Surv. India*, 1941, **75**.
Groves, A. W. .. *Quart. Jour. Geol. Soc. London*, 1935, **91**, 150.
Harker, A. .. *Metamorphism*, Methuen, 1932.
Hess, H. H. and Phillips, A. H. *Am. Mineral.*, 1938, **23**, 459.
———— .. *Ibid.*, 1940, **25**, 272.
Hess, H. H. .. *Ibid.*, 1949, **34**, 640.
Holland, T. H. .. *Mem. Geol. Surv. India*, 1900, 28–2.
Muthuswami, T. N. .. *Madras Uni. Jour.*, 1951, **21-B2**.
Poldervaart, A. .. *Min. Mag.*, London, 1947, **28**, 167.
Quensel, P. .. *Arkiv. Miner. Och. Geol.*, 1951, 1–10.
Rama Rao, B. .. *Mysore Geol. Dept. Bull.*, 1940, **17**, 70.
———— .. *Ibid.*, 1945, **18**.
Ramberg, Hans. .. *Journ. Geol.*, 1949, **57**-1, 36.
Stillwell, F. L. .. *Australian Antarctic Exped.*, 1911, **14**. *Sci. Repts. Ser.* A. **3**, pt. 1.
Turner, P. .. *Mem. Geol. Soc. America*, **30**, 102.
Vredenburg, E. W. .. *Jour. Asiatic Soc. of Bengal, N. S.*, 1948, **14**, 433.
Washington .. *Am. J. of Sc.*, 1916, 323.

EXPLANATION OF MICRO-PHOTOGRAPHS

1. Salite veins (Di) cutting across the hypersthene-salite intergrowth (IG).
2. Herring-bone structure of intergrowth (IG); Quartz (Q); Salite (Sa).
3. Hypersthene (Hy.) rim round ore; Salite (Sa).
4. Relicts of intergrowth (IG) and salite (Sa) in garnet.
5. Garnet (Ga) round ore; Plagioclase (Pl); Salite (Sa) and Quartz (Q).
6. Garnet (Ga) at contact of intergrowth (IG) and Plagioclase (Pl).
7. Biotite (Bi) shooting into plagioclase (Pl).
8. Amphibolization of garnet. Garnet (Ga); Hornblende (Ho); Spinel (Sp); Plagioclase (Pl).



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DIPOLE MOMENTS OF CAMPHOR COMPOUNDS*

Part II. The Dipole Moments of *dl*-Borneol, Camphoric Acid and 3-Bromo-Camphorenic Acid

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THE stereochemical characteristics of the camphor group present several interesting features and the present studies have been initiated as an approach to some aspects of the problem. One of us (P. T. N.) has reported the results with some camphor derivatives while the present communication deals with a further batch.

It has to be remarked here that, while extensive measurements of the dipole moments of the esters of dicarboxylic acids are available, the corresponding acids themselves do not appear to have received the same attention. The comparative insolubility of these compounds in nonpolar solvents has been the obstacle. However, camphoric acid, though insoluble in benzene, is sufficiently soluble in dioxan to permit of direct measurements on the free acid. Wilson and Wenzke (15) working with monocarboxylic acids report the absence of any association in this solvent but our experimental observations do not support this view. The results of observations on 3-bromocamphorenic acid in benzene provide a means for comparison with monocarboxylic acids.

LeFevre and Maramba (9) have recently reported on some peculiarities in the polarisations of antipodes in the terpene series and our results with borneol confirm these observations:

EXPERIMENTAL

Materials.—Benzene was purified as indicated in Part I (11); 1:4-*Dioxan* was purified by the method of Eigenberger (4). B.p. 101° C. (755 mm.) d_4^{35}: 1·01690 n_D^{35}: 1·4150: 2·1778;

d-Camphoric acid (Kahlbaum) was repeatedly purified by recrystallisation from absolute alcohol, m.p. (uncorr.) 187° C.

3-*Bromocamphorenic acid* was prepared by the method of Shive and co-workers (13). The final product after recrystallisation from benzene had a m.p. 181° C. (uncorr.).

* Based on thesis accepted for M.Sc. Degree of Madras University.

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dl-Borneol (B.D.H.) was recrystallised several times from absolute alcohol and then several times from pure benzene.

The final product had a m.p. of 212° C. (sealed tube). All measurements have been carried out in the same apparatus as described in Part I (*loc. cit.*)

RESULTS

The extrapolation method of Hedestrand was used in the computation of dipole moments from the data on dilute solutions. The atom Polarisation was assumed to be 5% of the molar refraction. All measurements have been made at 35° C. The results are presented in Tables I–III.

TABLE I

dl-Borneol in Benzene Solution

Mole fraction of solute $f_1 \times 10^6$	ϵ	d	αt_2	β
0	2·2535	0·86278	..	..
0·8070	2·2905	0·86430	4·584	0·218
1·1251	2·3048	0·86490	4·560	0·218
1·2370	2·3098	0·86515	4·552	0·222
1·7491	2·3331	0·86607	4·552	0·218
1·9760	2·3429	0·86651	4·524	0·219
$_TP_\infty$ = 116·5 c.c.		1·05 $_RM_D$ = 44·1 c.c. μ: 1·85 D		$_0P$ = 72·4 c.c.

TABLE II

3 *Br-Camphorenic Acid in Benzene Solution*

$f_1 \times 10^6$	ϵ	d	αt_2	β
0	2·2535	0·86278	..	..
1·386	2·2584	0·86431	3·535	1·280
4·405	2·2674	0·86725	3·148	1·176
5·204	2·2688	0·86805	2·940	1·174
7·597	2·2791	0·87016	3·370	1·126
9·251	2·2842	0·87227	3·319	1·189
10·530	2·2883	0·87350	3·305	1·180
$_TP_\infty$ = 103·85 c.c.		1·05 $_MR_D$ = 54·0 c.c. μ: 1·58 D		$_0P$ = 49·85 c.c.

TABLE III

d-Camphoric Acid in Dioxan Solution

Mole fraction $f_1 \times 10^6$	ϵ	d	αt_2	β
0	2·1778	1·01690	..	..
10·077	2·2813	1·02030	10·271	0·332
14·050	2·3190	1·02195	10·050	0·354
16·101	2·3320	1·02221	9·577	0·324
19·197	2·3503	1·02320	8·625	0·323

$_TP_\infty = 190{\cdot}7$ c.c. $\quad 1{\cdot}05\ {}_MR_D = 48{\cdot}3$ c.c. $\quad \mu = 2{\cdot}70$ D $\quad {}_0P = 142{\cdot}4$ c.c.

DISCUSSION

The dipole moment for *dl*-Borneol recorded here appears to be much higher than those reported by earlier workers. Donle and Wolf (3) reported 1·56 D for the *l*-variety while Higashi reported 1·65 D for the inactive form (8). Halverstadt and Kumler (6) have pointed out the possible errors in working with high dilutions but we have to presume the absence of these since both dielectric constant and density values show a strictly linear relationship with the concentration in our observations, leading to the limiting value for the pure solvent in each case. The discrepancy has then to be traced to other causes. As has been indicated in Part I as well as in the work on Pyran compounds (Anantakrishnan and Soundararajan, 1), greater accuracy can be claimed now both for the extrapolation methods used and for the experimental set-up. Another possible cause of discrepancy is the difference in the concentration range used. Higashi's work uses the molefraction range 0·0283 to 0·0822 while the present work is with the more dilute solution with the molefraction range 0·00807 to 0·01976.

Using tartrates as examples, Cotton (2) has shown that in water salts of racemic acid are different from equivalent mixtures of the two tartrates and one may expect a similar state of affairs with other optically active compounds as has been shown to be the case by LeFevre and Maramba (*loc. cit.*). In the present case one may legitimately expect that even in benzene solution we are dealing with an equilibrium

$$(+\ -) \rightleftharpoons (+) + (-)$$

in which the position may be slightly shifted with temperature. If association between the antipodes takes place, the apparent polarisation at any

given concentration of the racemate will be different from that of the single component. Taking these into account, one can readily account for the differences noticed. Further work with the pure components and over a larger range of concentration as well as of temperature is needed before the phenomenon can be understood.

The carboxylic acids are of interest from a different angle. The cyclohexane ring in camphor is known to be multiplanar, having the " boat " form and the bridge is also not in the same plane but the position may not be the same in the products of oxidation. In 3-Bromo camphorenic acid we have to consider the interaction of moments due to the presence of a double bond, the bromine atom and the carboxylic group while in camphoric acid we have the mutual interaction of two carboxyl groups attached to 1 : 3 carbon atoms. As indicated earlier, we have the further complication in the latter case of having dioxan as the solvent.

In the present state of our knowledge of group interactions, evaluation of the dipole moment of the bromocamphorenic acid from group moments and mesomeric moments is not feasible but one may expect the value to be less than that of bromocyclohexane but more than that of cyclohexane carboxylic acid and the value observed is in this range.

From the stereochemical configuration of camphor, known from physical evidence, one may expect at least three different forms for camphoric acid but the form that is generally obtainable is one which readily forms an anhydride and can reasonably be presumed to have both carboxylic acid groups on the same side of the plane of the cyclopentane ring. This is further indicated by the large dipole moment observed. While this qualitative conclusion can be drawn, the actual value of the moment is liable to two sources of error. Solvent solute association can vitiate results and as indicated by Sutton (14) where large moments are involved the assumption that atom polarisation is small cannot be justified.

Wilson and Wenzke (*loc. cit.*) observe from the measurements on the dipole moments of monocarboxylic acids in dioxan that the values approximate to those in the gaseous phase. They consider that as a solvent containing oxygen in its structure, it is able to break up the hydrogen bonds of the acid molecules, thereby leading to the values of the monomer. It is implicit here that there is interaction between solvent and solute. Further, Haggis has clearly shown that in hydrogen bonded substances, solvent solute reaction is invariably present (5). Our results in Table III show that the value of $^{\varepsilon}\alpha$ varies inversely as the concentration of the camphoric acid. This is a clear indication that there is interaction between

dioxan and the acid, besides a possible intermolecular association. The moment observed is probably that of the complex rather than the monomer and the coincidence observed by Wilson and Wenzke may be fortuitous (*cf.*, also LeFevre and Vine, 10).

The evidence from measurements of relaxation times is also not definite. Potopenko and Wheeler (12) from measurements on monocarboxylic acids in dioxan conclude that τ dioxan is uninfluenced by these solutes while Haggis (*loc. cit.*) using water as the solute draws a different conclusion. It is clear that fuller investigations on both dipole moments and relaxation times in dioxan and other solvents with mono and dicarboxylic acids as solutes is necessary. We can, however, safely consider that, taking the trend in values, dioxan solutions depart from ideal behaviour and as such the moment values cannot be the same as that in the gas phase.

One of us (P. T. N.) has to thank the University of Madras for a studentship which enabled him to take part in these studies. Our thanks are also due to Dr. M. A. Govinda Rau for valuable suggestions.

Summary

Dipole moment measurements on *dl*-borneol, 3-bromocamphorenic acid and camphoric acid are reported. The results with dilute solutions of *dl*-borneol indicate a possible independent existence of the antipodes in very dilute solutions besides the racemic form. The values for camphoric acid in dioxan demonstrate the presence of solvent-solute interactions in this solvent.

References

1. Anantakrishnan and Soundararajan, S. .. *Proc. Ind. Acad. Sci.*, 1953, **37**, 578.
2. Cotton .. *Trans. Farad. Soc.*, 1930, **26**, 377.
3. Donle, H. C. and Wolf, K. L. .. *Z. Physik. Chem.*, 1930, **8** B, 55.
4. Eigenberger, E. .. *J. Pr.*, 1931, **130**, 75.
5. Haggis, G. H. .. *J. Chem. Phys.*, 1952, **20**, 1461.
6. Halverstadt, I. F. and Kumler, W. D. .. *J. A.C.S.*, 1942, **64**, 2988.
7. Hedestrand, G. .. *Z. Phys. Chem.*, 1929. **2** B, 428.
8. Higashi, K. .. *Bull. Inst. Phys. Chem. Japan*, 1932, **11**, 729.
9. LeFevre and Maramba, F, .. *J. C. S.*, 1952, 235.
10. LeFevre, R. J. W. and Vine, H. H. *Ibid.*, 1938, 1795.
11. Narasimhan, P. T. .. *Proc. Ind. Acad. Sci.*, 1953, **37**, 551.
12. Potapenko, G. and Wheeler, D. .. *Rev. Mod. Physics*, 1948, **20**, 143.
13. Shive, B., *et al.* .. *J.A.C.S.*, 1941, **63**, 2979.
14. Sutton, L. E. .. *Ann. Report*, 1940, 37, 53, 63.
15. Wilson, C. J. and Wenzke, H. H. *J. Chem. Phys.*, 1934, **2**, 546.

CHONDRODITE FROM THE CALC-SILICATE ROCKS OF LATEHAR, PALAMAU DISTRICT

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Introduction

Chondrodite has been reported from a few localities in India, but a detailed study of the mineral has not been made. It is partly due to the fact that many of the discoveries of the mineral in India date back to a period when microscopic work was not advanced and hence only a reference to the occurrence of chondrodite has been made, in describing mostly the economic deposits of an area. The occurrence of chondrodite has been mentioned while describing the corundum localities of Salem and Coimbatore Districts (Middlemiss, 1896) the pyroxenic gneiss and scapolite-bearing rocks of Ceylon and Salem (Lacroix, 1891) and the petrology and manganese ore deposits of the Sausar Tahsil, Chhindwara District (Fermor, 1906). Pande and others (1947) have not noted the occurrence of calc-silicate rocks associated with the marble of the area nor have they observed chondrodite in the marble. A preliminary note on the occurrence of chondrodite in the calc-silicate rocks of Latehar was communicated by the authors to the 39th session of the Indian Science Congress (Proc. Pt. III, Abstracts, p. 169, 1952). Since then, the senior author has re-examined fully the material, together with more sections sliced from the rocks and has determined the mineralogical and optical characters of the constituent minerals. The results of this investigation which form the subject of this paper deal with the description of the occurrence and origin of chondrodite in the forsterite marbles of Latehar.

Occurrence

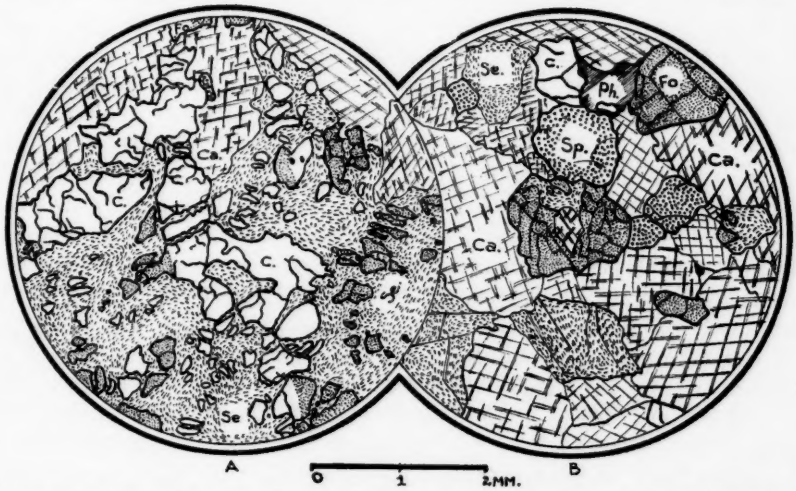
The marbles and the associated calc-silicate rocks occur as inclusions in the granite gneiss of the area. Excellent exposures of these rocks are seen along the Dhardhari Nala near the villages Kothila and Kodag, a mile or a mile and half south-west of Latehar, and also south of Auranga river near Bhagwanpur village. In the Dhardhari Nala section a complete gradation from the marbles to the calc-silicate rocks can be observed. The Nala Section close to the contact of the granite gneiss shows a thin band of

diopside-phlogopite-microcline rock followed by forsterite marble with chondrodite and spinel, white crystalline limestone and calc-silicate hornfels. These localities are easily accessible from Latehar.

Petrography of the Chondrodite-bearing Marbles

In hand specimen, the typical rock shows yellowish green serpentine set in a matrix of calcite. Near the contact of the granite gneiss, the rock is coarsely crystalline and in addition to serpentine carries deep orange or honey yellow chondrodite, pale lavender grey spinel and a very pale brownish mica. The proportion of spinel and chrondrodite in the rock is much variable, thus while some specimens show only a few scattered grains, there are others which are crammed with these minerals and such rock specimens can be aptly called chondrodite-spinel-forsterite marble. Besides the pale violet variety of spinel, small octahedra of magnetite having good crystal faces and lustre of polished steel are often present in these rocks.

In thin sections, the rhombohedral carbonate is seen to be the dominant constituent forming about 60% of the rock. It is mostly *calcite*, and occurs usually as turbid allotriomorphic and interlocking grains. *Dolomite* is very subordinate and it is similar in shape, size and turbidity to calcite, but is easily distinguished from the latter by the silver chromate test. *Forsterite* occurs either as clear and small ovoid grains set in calcite or as large grains split up into numerous small islands by the invading stringers of serpentine (Text-Fig. 1 A). Idioblastic forsterite showing hexagonal outline is rare.



Text-Fig. 1. Chondrodite in the calc-silicate rocks of Latehar. *C.*, Chondrodite; *Fo.*, Forsterite, *Ph.*, Phlogopite; *Se.*, Serpentine; *Ca.*, Calcite; *Sp.*, Spinel; and solid black iron ore.

Forsterite is optically positive, shows high relief, strong birefringence and large 2 V. Pale green *serpentine* and pale green to colourless *antigorite* occur as pseudomorphs after forsterite and are evenly distributed in the slides. Antigorite is optically negative and shows weak birefringence. *Spinel* is almost colourless, generally rounded but occasionally idioblastic showing an octahedral outline. It shows very high relief and is completely isotropic. *Phlogopite* is colourless, prismatic or irregular in outline and shows fine cleavage lines, strong birefringence, straight extinction and a small 2 V. *Diopside* is colourless, subhedral, optically biaxial positive and shows $Z' \wedge c = 37°$. Along the margin it shows alteration to greenish serpentine. *Tremolite* occurs as long bladed prismatic sections showing medium birefringence and $Z' \wedge c = 17°$. Occasionally, a little *chlorite* (*clinochlore*) is seen. Granular *magnetite* is observed. *Sphene* occurs as grains, granules or patches associated with chondrodite. It is grayish pink in colour and pleochroic from pale greenish grey to brownish pink. It has strong refringence and bifrefringence. Rarely it occurs as inclusions in the chondrodite (Plate XLVI, Fig. 1) and in one case (D/14,2876), granular sphene occurs cutting the twinning lamellæ of chondrodite. This shows that the chondrodite is earlier in origin than the sphene. Anhedral grains of yellow *chondrodite* occur in close association with spinel and forsterite olivine (Text-Figs. 1, A and B). Occasionally chondrodite shows a subhedral outline. The amount of chondrodite is so variable that in some slices of the rock it is either absent or limited to one or two grains whereas in others it is so abundant as to form an essential constituent. The cleavages are imperfect and in the best example $X' \wedge 001 = 26° \pm 2°$. Twinning is fairly common on (001) and it appears to be on one law and may be simple or lamellar. Simple twinning seems to be the common type. One grain (Slide No. D/14,2876) in addition to the (001) twinning shows another twinning which may be on (305). This suggestion is made by the close similarity exhibited by the twinned grain with one figured by Von Eckermann from Mansjö Mountain, Sweden (1922, Fig. 99, plate 57). In the later type of twinning [along (305)], which is of rarer occurrence, twinning formation is observed in patches. The twinning lamellæ are of varying width and are narrowed down step-wise and abruptly broken off (Plate XLVI, Fig. 2). Chondrodite has a well marked body colour and is strongly pleochroic. The scheme is X = golden yellow, Y = pale yellow or colourless and Z = pale yellow or colourless. The absorption formula is $X > Y = Z$. Chondrodite shows high relief with $Ng = 1{\cdot}643 \pm {\cdot}002$, $Nm = 1{\cdot}623 \pm {\cdot}002$ and $NP = 1{\cdot}610 \pm {\cdot}002$ (determined on the cleavage flakes by the immersion method using Leitz-Jelley Mikro-refraktometer). Birefringence is fairly strong with

Ng — Np = ·033 ± ·002. It is optically biaxial positive. The optic axial angle is 74° ± 1 determined on the Universal Stage by direct measurement applying E. Tröger's correction (C. Burri, 1951, Table IV, p. 296). The pleochroism of the mineral is not uniform, thus while one portion of the individual is strongly pleochroic another portion of the same crystal is weakly pleochroic or almost colourless. Chondrodite is much fissured by cracks and very frequently it shows alteration into antigorite or serpentine. Thin veins of fibrous antigorite are seen replacing the chondrodite (Plate XLVI, Fig. 3). In some places where the chondrodite shows a greater degree of alteration, the remains of unaltered chondrodite occur within antigorite or serpentine as islands and the entire process of transformation is completely analogous to that of forsterite, to which it bears a bewildering resemblance (Text-Fig. 1, A). It is also observed at places that a part of the crystal is forsterite olivine and the remaining part is chondrodite and the two are found in the same crystal without any definite boundary showing thereby that the forsterite olivine is being gradually transformed into chondrodite (Text-Fig. 1, A).

Chondrodite more or less similar in properties and occurrence to the Latehar chondrodite has been described by Lacroix (1891) from the cipolins of Ceylon, by Bleek (1908) from the crystalline limestone of kachin hills, Burma, by Fermor (1906) from the serpentine marble of Chhindwara District, Madhya Pradesh, by Middlemiss (1896) from the corundum-bearing rocks of Salem and Coimbatore Districts, by Hayden (1911) from the Jagdallak marble of Northern Afhganistan, by Read and Double (1935) from the Glenelg limestone of Inverness-shire and by Eckermann (1922) from the limestones of Mansjö Mountain. The optical properties of the chondrodites of Mansjö Mountain (*loc. cit.*) and Glenelg (*loc. cit.*) have been tabulated in Table I, because the chondrodites of these area have been investigated in great detail. The optical properties of Latehar chondrodite is also given in Table I, for comparison and ready reference.

It is observed from Table I that the optical properties of the Latehar chondrodite are almost similar to those of the G-chondrodite of Mansjö Mountain, Sweden, described by Eckermann (*loc. cit.*) and Glenelg chondrodite described by Read and Double (*loc. cit.*) by its twinning, optic sign, optic axial angle, refringence, birefringence and pleochroism. There is a slight difference in the refringence and birefringence between the chondrodite of Latehar, Glenelg and Mansjö Mountain. This might be possibly due to the varying replacement of Mg by Fe and varying hydroxyl tenor in the composition of the chondrodites of the above areas (Winchell, 1945). In occurrence and association as well, the Latehar chondrodite shows good

TABLE I

Optical Properties of Chondrodite

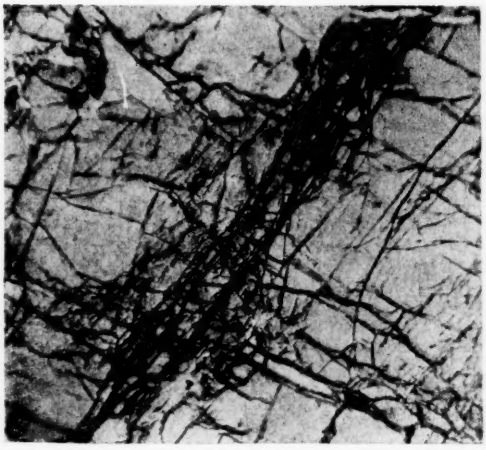
		Mansjö Mountain (G-Chondrodite) H. Von Eckermann	Glenelg, Inverness-shire Read and Double	Latehar, Palamau Sadashivaiah and Ghosh
X or X′ ∧ 001		26° 25′	30°	26° ± 2
Twinning		on (001) and (305) simple and lamellar	on (001) and (305) Simple and lamellar	on (001) and (305) simple and lamellar
Optic Sign		Biaxial Positive	Biaxial Positive	Biaxial Positive
Ng	=	1·643	1·639	1·643 ± ·002
Nm	=	1·620	..	1·623 ± ·002
Np	=	1·607	1·610	1·610 ± ·002
Ng—Np	=	0·036	0·029	0·033 ± ·002
Pleochroism:—				
X	=	Brownish Yellow	Bright Yellow	Golden Yellow
Y	=	Light Yellow	Faint Yellow or colourless	Pale Yellow or colourless
Z	=	Yellowish White	Faint Yellow or colourless	Pale Yellow or colourless
Absorption		X > Z > Y	X > Y = Z	X > Y = Z
2 V		72° 14′	72°–74′	74° ± 1°

resemblance to the Glenelg and Mansjö Mountain chondrodites. At all these localities chondrodite occurs in the marbles associated with various calc-silicates. The resemblance is most striking especially in the case of Glenelg chondrodite because at both the localities chondrodite occurs in the orsterite marbles associated chiefly with calcite, forsterite, antigorite (serpentine), phlogopite, diopside, chlorite and iron ore.

CONCLUSION

Chondrodite thus occurs in the forsterite marbles around Latehar. Chondrodite is universally present in this limestone though varying in amount. In characters, occurrence and association, the Latehar chondrodite closely resembles the G-chondrodite of Mansjö Mountain, Sweden, and Glenelg chondrodite of Inverness-shire. The occurrence of Latehar chondrodite as granules and patches partially replacing forsterite-olivine suggests that the chondrodite has been produced by the pneumatolytic metasomatism from forsterite by the accession of fluorine and hydroxyl-bearing fluids from the magmatic liquids which gave rise to the neighbouring granite gneiss of

1



2

3

the area. A more or less similar view has been expressed by Read and Double and Eckermann in their study of the Glenelg and Mansjö Mountain chondrodites respectively.

Acknowledgements

The authors wish to thank Prof. N. L. Sharma and Dr. P. R. J. Naidu for suggestions and facilities given during the course of the investigation.

References

1. Bleek, A. W. G. .. "Rubies in the Kachin Hills, Upper Burma," *Rec. G. S.I.*, 1908, **36**, Pt. 3, 167.
———— .. "Jadeite in the Kachin Hills, Upper Burma," *Ibid.*, 1908, **36**, Pt. 4, 267.
2. Burri, C. .. "*Das Polarisations Mikroskop.*, 1951, 296.
3. Eckermann, H. Von. .. "The Rocks and contact minerals of the Mansjö Mountain", *Geol. Fören. Forh. Stockholm*, 1922, **33**, Pt. 3, 379–83.
4. Fermor, L. L. .. "Notes on the petrology and manganese ore deposits of the Sausar Tahsil, Chhindwara District", *C. P. Rec. G. S. I.*, 1906, **33**, Pt. 3, 204.
5. Hayden, H. H. .. "The Geology of Northern Afganisthan", *Mem. G. S. I.*, 1911, **39**, Pt. 1, 12.
6. Lacroix, M. Al. .. "Contributions to the study of the pyroxenic varieties of gneiss and of the scapolite-bearing rocks of Ceylon and Salem," *Rec. G. S. I.*, 1891, **34**, Pt. 3, 194.
7. Middlemiss, C. S. .. "Preliminary notes on some corundum localities in the Salem and Coimbatore Districts, Madras," *Ibid.*, 1896, **39**, Pt. 2, 41.
8. Pande, I. C., Agrawal, S. K. and Tewari, B. S. "A contribution to the geology of Latehar, Palamau District, Bihar," *Quart. Journ. Geol. Min. Met. Sec. Ind.*, 1947, **19**, No. 1, 7–14.
9. Read, H. H. and Double, I. S. "On the occurrence of Chondrodite in the Glenelg limestone of Inverness-shire", *Min. Mag.*, 1935, **14**, No. 149, 84–9.
10. Sadashivaiah, M. S. and Ghosh, S. D. .. "Occurrence of Chondrodite in the Calc-Silicate Rocks of Latehar, Palamau District," *Proc. Ind. Sci. Cong.*, 1952, Abstracts, Pt. 3, 169.
11. Winchell, A. N. .. *Elements of Optical Minerology*, 1945, Pt. 2, 196.

Explanation of Plate

Fig. 1. Calc-silicate rock (No. V 417/2) containing chondrodite (*C*), spinal (*Sp*), sphene (*S*), and phlogopite (*Ph*), in a matrix of calcite (*Ca*). × 16. Ordinary light.

Fig. 2. Thin veins of fibrous antigorite replacing chondrodite (No. D/14). × 16. Ordinary light.

Fig. 3. Chondrodite showing the twinning lamellæ of varying width, which are narrowed dow step-wise and abruptly broken off.
(No. D/14). × 16. Crossed nicols.

CHEMISTRY OF THE THIAZOLES

IV. Bromination and Nitration of Some Monosubstituted Thiazoles

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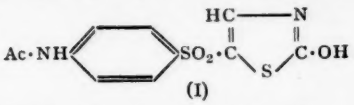
Certain gaps at present exist in the data on the orientation of the incoming group on substitution in the case of some monosubstituted thiazoles. To fill this up, we have attempted the bromination and nitration of the three isomeric methylthiazoles, 2-hydroxythiazole, 2-methoxythiazole and 5-acetamidothiazole. The results obtained are presented here. The significance of these in the light of our present knowledge would be discussed in the succeeding paper.

2-Methylthiazole does not undergo substitution with ease. On bromination, it furnished a bromo compound, presumably 2-methyl-5-bromothiazole. Babo and Prijs[1] nitrated 2-methylthiazole at 330° C. and obtained 2-methyl-5-nitrothiazole in about 4 per cent. yield. We had obtained the same nitro compound in about the same yield by carrying out the nitration at 110° C. 4-Methylthiazole could not be brominated at all even on heating the reactants at 110° C. for 12 hours. Ochiai[2] first reported that 4-methylthiazole could not be nitrated but Nagasawa[3] has obtained a mononitro compound, m.p., 57·5° C., the yields not being stated. We have nitrated 4-methylthiazole at 100° C. (12 hours) to obtain the same nitro compound in about 30 per cent. yields, which has been proved to be 4-methyl-5-nitrothiazole by Erlenmeyer *et al.*[4] since it is different from 4-methyl-2-nitrothiazole (m.p., 36–8°) prepared by them from 2-amino-4-methylthiazole. 5-Methylthiazole on bromination furnished 2-bromo-5-methylthiazole in good yields. The structure of this has been confirmed by the fact that on treatment with sulphanilamide it furnishes 2-sulphanilamido-5-methylthiazole. On nitration, 5-methylthiazole furnished a mononitro compound, m.p. 110° C., which should be 5-methyl-4-nitrothiazole because it is different from 5-methyl-2-nitrothiazole reported by Erlenmeyer *et al.*[4]

2-Hydroxythiazole was prepared by the action of ammonium thiocarbamate on chloracetaldehyde and this compound is identical with that obtained by Ganapathi and Venkataraman[5] as a byproduct in the preparation of 2-halogenothiazole from 2-aminothiazole by diazotisation and Sandmeyer's reaction. On bromination it furnished a monobromo compound, m.p.

67° C., which we consider to be 2-hydroxy-5-bromothiazole; it furnished with potassium acetamido phenylsulphinate, the corresponding sulphone (I).

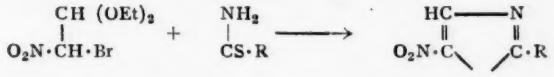


(I)

Since the 4-bromothiazoles do not react, we assign the structure of 2-hydroxy-5-bromothiazole for the bromination product. On nitration, 2-hydroxy thiazole easily furnishes a nitrothiazole, m.p. 146–7° C., which is identical with that obtained by Ganapathi and Venkataraman[6] by the hydrolysis of 2-bromo-5-nitrothiazole. On treatment with acetic anhydride, 2-hydroxy-thiazole yields an acetyl derivative; since this dissolves in alkali, this is not an O-acetyl compound. We assign it the structure of 2-hydroxy-5-acetyl-thiazole. This compound also reacts very vigorously with phosphorus oxychloride indicating the presence of the hydroxy group. All the above-mentioned 2-hydroxythiazoles are not stable. They do not keep on standing but undergo polymerisation or decomposition and turn dark, as is expected.

Treatment of 2-bromothiazole with sodium methoxide furnished 2-methoxythiazole, b.p. 142–6° C. in good yields. It gets nitrated easily with a mixture of nitric acid and sulphuric acid at the room temperature, furnishing a compound, m.p. 59°, which we take to be 2-methoxy-5-nitrothiazole. On bromination of 2-methoxythiazole, we also obtain a bromo compound which we consider to be 2-methoxy-5-bromothiazole.

Attempts to synthesise 5-nitro-2-hydroxythiazole and 5-nitro-2-methyl-thiazole by the action of $\alpha:\alpha'$-bromonitroacetal on ammonium thio-carbamate and thioacetamide respectively as follows:

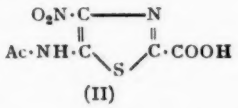


were not successful. We expected to fix up the orientation of the nitrated products by the above synthesis.

After our work on the nitration and bromination of 5-acetamidothiazole was completed, the paper by Prijs, Mengisen Fallab and Erlenmeyer[7] appeared. As reported by Prijs *et al.*,[7] we also find that bromination of 5-acetamido-thiazole always leads to the dibromo derivative. Using even less than one molecular equivalent of bromine did not furnish the mono bromo derivative. To prepare the mono bromo derivative, we brominated 5-acetamidothiazole-2-carboxylic acid and obtained surprisingly enough only 5-acetamido-2:4-dibromothiazole. So, just as it happens in the thiophene derivatives, there was decarboxylation and bromination. Prijs *et al.*[7] have however been

successful in preparing the mono bromo derivative by the use of N-bromo-succinimide.

Nitration of 5-acetamidothiazole furnished in our hands a nitro derivative, m.p. 197–8° C., which Prijs *et al.*[7] describe as a dinitro derivative. But we find it to be only a mono nitro compound, with the structure 5-acetamido-4-nitrothiazole. Conclusive proof was obtained by nitrating 5-acetamidothiazole-2-carboxylic acid to 5-acetamido-4-nitrothiazole-2-carboxylic acid (II), m.p. 155–6°, and decarboxylating it to a compound identical with the nitration product of 5-acetamidothiazole.



(II)

Two things are of interest to note in this connection. While the bromination of 5-acetamidothiazole-2-carboxylic acid leads to decarboxylation, nitration does not effect this. While 5-acetamidothiazole-2-carboxylic acid is easily nitrated and brominated, Ganapathi and Venkataraman[8] could not nitrate 2-acetamidothiazole-4-carboxylic acid and 2-acetamidothiazole-5-carboxylic acid, in spite of the fact that the position 5 in the first compound was free.

The significance of the findings presented here are discussed in the succeeding paper.

EXPERIMENTAL

2-Methyl-5-nitrothiazole.—2-Methylthiazole (15·0 g.) was gradually added to a cooled mixture of fuming sulphuric acid (50 c.c.) and fuming nitric acid (40 c.c.), the mixture kept overnight, heated on the steam-bath for 10 hours and then at 120° C. in an oil-bath for 4 hours. The liquid after cooling was poured on ice when a white solid was thrown down. The aqueous mixture was extracted with ether, and the solvent removed from the extract whereby 2-methyl-5-nitrothiazole was obtained (yield, 0·78 g.). It crystallised from petroleum-ether and had m.p. 129–31° C. (Found: N, 19·1; $C_4H_4O_2N_2S$ requires N, 19·4 per cent.).

2-Methyl-5-bromothiazole.—2-Methylthiazole (5 g.) in acetic acid (10 c.c.) was treated with bromine (8 g.). The mixture was allowed to stand-overnight, heated on the steam-bath for 10 minutes, poured on ice water, the mixture made alkaline with sodium bicarbonate and extracted with ether. After removal of the solvent, the bromothiazole was distilled. It passed over at 148–56° (yield, 3·45 g.) (Found: N, 7·78; C_4H_4NSBr requires N, 7·86 per cent.). The bromo compound did not form a picrate.

4-*Methyl*-5-*nitrothiazole*.—4-Methylthiazole (6·0 g.) was added gradually to fuming sulphuric acid (15 c.c.) followed by potassium nitrate (6·0 g.), maintaining the temperature between 20–30° C. The mixture was kept overnight at room temperature, heated on the steam-bath for 24 hours, cooled and poured on ice. The mixture was neutralised with sodium carbonate and then extracted with ether. After removal of the solvent a crystalline solid was obtained (3·0 g.) which on recrystallisation from petroleum-ether had m.p. 58–9° C. (Found: N, 19·24; $C_4H_4O_2N_2S$ requires N, 19·44 per cent.). The nitro compound dissolves in dilute sodium hydroxide solution to give a yellow solution which readily turns deep red. It did not yield a picrate.

5-*Methyl*-4-*nitrothiazole*.—5-Methylthiazole (4·0 g.) was added slowly to fuming sulphuric acid (15 c.c.) followed by potassium nitrate (4·0 g.) maintaining the temperature between 20° and 30° C. by cooling. After keeping overnight, it was heated on the steam-bath for 12 hours, cooled and poured on ice. The mixture was neutralised with sodium carbonate and then extracted with ether. After removal of the solvent, a crystalline solid resulted (2·5 g.) which crystallised from petroleum-ether in shining plates and had m.p. 110° C. (Found: N, 19·12; $C_4H_4O_2N_2S$ requires N, 19·44 per cent.). The product dissolves in dilute sodium hydroxide with a red colour which darkens on keeping. It did not form a picrate.

2-*Bromo*-5-*methylthiazole*.—To 5-methylthiazole (5·0 g.) taken up in acetic acid (10 c.c.), bromine (8·2 g.) was added slowly with good cooling, the mixture allowed to stand overnight, poured on ice water, made alkaline with sodium carbonate and then extracted with ether. After dehydrating the ethereal solution (sodium sulphate), the solvent was removed. The residual 2-bromo-5-methylthiazole distilled at 192–200° C. (yield, 5 g.) and appears to be identical with that prepared by Ganapathi and Venkataraman[5] from 2-amino-5-methylthiazole.

2-p-*Aminobenzenesulphonamido*-5-*methylthiazole*.—The foregoing bromo-compound (4 g.), sulphanilamide (4 g.), anhyd. potassium carbonate (2 g.) and copper bronze (0·5 g.) were intimately mixed and heated in the oil-bath at 120° C. for one hour. The dark coloured fused mass was triturated with sodium hydroxide filtered, and the filtrate neutralised with hydrochloric acid. The precipitate obtained was collected and crystallised from alcohol (yield, 2·5 g.), m.p. 245–47° (Found: N, 15·51; $C_{10}H_{11}N_3O_2S_2$ requires N, 15·61 per cent.). This product was identical with an authentic sample obtained by the hydrolysis of 2-acetsulphanilamido-5-methylthiazole in turn prepared by the condensation of 2-amino-5-methylthiazole and acetsulphanilyl chloride in pyridine.

2-*Hydroxythiazole.*—Freshly prepared ammonium thiocarbamate (23 g.) was dissolved in water (15 c.c.) and freshly distilled chloracetaldehyde (19 g.) was added gradually with cooling and stirring. The reaction mixture was then kept in the refrigerator overnight. 2-Hydroxythiazole separated as a brown solid was collected (3 g.) and crystallised from alcohol; m.p. 69–70° (Found: N, 14·1; C_3H_3ONS requires N, 13·86 per cent.). 2-Hydroxythiazole on keeping darkens and probably polymerises. It forms a red dye when coupled with diazotised *p*-toluidine.

2-Hydroxy-5-bromothiazole.—2-Hydroxythiazole (2 g.) was dissolved in chloroform (10 c.c.) and bromine (3·2 g.) was added to it gradually with good shaking and under external cooling. The reaction mixture was then kept in the ice-box for 3 to 4 hours when a yellowish solid (1·5 g.) with deep penetrating odour separated. It was separated and purified by dissolving it in alcohol and adding water; m.p. 67° (dec.) (Found: N, 7·3; C_3H_2ONSBr requires N, 7·7 per cent.). The bromo compound is not very stable and decomposes on standing.

4-*Acetamidophenyl*-(2′-*hydroxy*) *thiazolyl* (5)-*sulphone.*—An intimate mixture of the foregoing bromo compound (3 g.), potassium *p*-acetamidobenzene sulphinate (4 g.), copper bronze (0·1 g.), trace of iodine and propylene glycol (15 c.c.) was maintained at 100° C. for about 6 hours and then poured on ice. A solid separated along with some tar. The solid matter was separated, washed with water and crystallised from dilute alcohol (0·8 g.); m.p. 263–64·5° (dec.). The product was soluble in alkali (Found: N, 8·9; $C_{11}H_{10}O_4N_2S_2$ requires N, 9·3 per cent.).

2-*Hydroxy*-5-*nitrothiazole.*—To a cooled mixture of con. sulphuric acid (10 c.c.) and con. nitric acid (4 c.c.) was added 2-hydroxythiazole (4 g.) in small portions under external cooling. After completion of addition, the mixture was kept in the ice-chest for 3 hours and then at room temperature for 1 hour. On pouring it on ice, a yellowish brown precipitate was thrown out, which was filtered and crystallised from dilute alcohol; 2-hydroxy-5-nitrothiazole separated in yellowish needles, m.p. 146–7° C. (yield, 1·5 g.) (Found: N, 19·0; $C_3H_2O_3N_2S$ requires N, 19·1 per cent.). It is identical with the product prepared by Ganapathi and Venkataraman by boiling 2-bromo-5-nitrothiazole with dilute sulphuric acid. It dissolves in alkali with red coloration.

2-*Hydroxy*-5-*acetylthiazole.*—2-Hydroxythiazole (3 g.) was dissolved in pyridine (5 c.c.) and acetic anhydride (10 c.c.) was added to it, the reaction mixture kept overnight and next day heated on the steam-bath for 3 hours. The excess of acetic anhydride and pyridine were removed under vacuum

by distillation and the residual pasty mass treated with ice. The solid that separated was filtered, washed and crystallised from alcohol (yield, 0·8 g.); m.p. 195–7° C. (Found: N, 9·4; $C_5H_5O_2NS$ requires N, 9·8 per cent.). It dissolves in alkali and reacts with phosphorus oxychloride.

2-*Methoxythiazole*.—2-Bromothiazole (18 g.) was added gradually to sodium methoxide (prepared from sodium, 2·5 g., and methyl alcohol, 70 c.c.) and refluxed for 20 hours on the steam-bath. The reaction mixture was diluted with ether, the separated sodium bromide filtered off, and the solvent removed from the filtrate. The residual 2-methoxythiazole on distillation passed over at 142–46° C. (yield, 12 g.) It gave a picrate, m.p. 90° C. (Found: N, 16·1; $C_{10}H_8O_8N_4S$ requires N, 16·2 per cent.).

2-*Methoxy*-5-*nitrothiazole*.—2-methoxythiazole (7·5 g.) was added gradually to a cooled mixture of con. sulphuric acid (30 c.c.) and con. nitric acid (8 c.c.) and the reaction mixture allowed to stand overnight. On pouring on ice the nitro compound was thrown out which crystallised from petroleum-ether (3·5 g.), m.p. 59° (Found: N, 17·67; $C_4H_4O_3N_2S$ requires N, 17·5 per cent.). The nitro compound gives a yellow coloration in dilute sodium hydroxide.

5-*Acetamido*-4-*nitrothiazole*.—5-Acetamidothiazole (0·5 g.) was slowly added to concentrated sulphuric acid (4 c.c.) under cooling; to this con. nitric acid (2 c.c.) was gradually added and the reaction mixture allowed to stand overnight. On pouring the clear solution on ice, the nitro compound separated, which was filtered off, washed (0·25 g.) and crystallised from alcohol; m.p. 197–8° (Found: N, 22·1; $C_5H_5O_3N_3S$ (mono nitro derivative) requires N, 22·4 per cent.; $C_5H_4O_5N_4S$ (dinitro compound) requires N, 24·1 per cent.). This nitro compound dissolved in sodium hydroxide solution with a red colour.

(ii) 5-Acetamido-4-nitrothiazole-2-carboxylic acid (prepared as described below, 1 g.) was maintained at 160–70° C. till there was no more evolution of carbon dioxide. On crystallising the residual mass from acetone was obtained the nitro compound (0·3 g.) as a crystalline powder, m.p. 197–8° (Found: N, 22·0; $C_5H_5O_3N_3S$ requires N, 22·4 per cent.). This compound is identical with that described above and obtained by the nitration of 5-acetamidothiazole.

5-*Acetamido*-4-*nitrothiazole*-2-*carboxylic acid*.—5-Acetamidothiazole-2-carboxylic acid (1 g.) was added in portions to con. sulphuric acid (8 c.c.) followed by con. nitric acid (2 c.c.) and the reaction mixture was allowed to stand overnight. On pouring the solution on ice, a solid separated which was filtered, dissolved in dilute sodium bicarbonate solution and precipitated

by acid (0·5 g.). On crystallisation from alcohol the nitro compound had m.p. 155–56° (dec.), solidified and again melted at 189–92° (Found: N, 17·8; $C_6H_5O_5N_3S$ requires N, 18·1 per cent.).

5-*Acetamido*: 2: 4-*dibromothiazole.*—5-Acetamidothiazole (1 g.) was dissolved in acetic acid (6 c.c.) and to this was added bromine (1·3 g.). The mixture was allowed to stand overnight, poured on ice, and the mixture neutralised with sodium bicarbonate, when the bromo compound separated as a dark brown mass. On crystallisation from alcohol (0·8 g.), the dibromo compound had m.p. 148–49° (Found: N, 9·3; $C_5H_4ON_2SBr_2$ requires N, 9·3 per cent.). Even by using less than half the amount of bromine the same dibromo compound was obtained.

(ii) To 5-acetamidothiazole-2-carboxylic acid suspended in chloroform (20 c.c.) was added bromine (1·2) with external cooling in ice water, the reaction mixture allowed to stand overnight. The excess of bromine was removed with sodium sulphite, the chloroform solution separated, and the solvent removed. The residual brown solid mass was triturated with dilute sodium bicarbonate solution, which was found to extract the unreacted starting material. The product that did not dissolve in bicarbonate (0·8 g.) on crystallisation from acetone had m.p. 148–49° (Found: N, 9·3; $C_5H_4ON_2SBr_2$ requires N, 9·3 per cent.) and was found to be identical with 5-acetamido: 2: 4-dibromothiazole described above.

We thank Mr. M. H. Shah, Microanalyst, for carrying out the analyses reported in this paper.

SUMMARY

In connection with the study of the orienting influences in the thiazole nucleus, 2-methylthiazole, 4-methylthiazole, 5-methylthiazole, 2-hydroxythiazole, 2-methoxythiazole, 5-acetamidothiazole and 5-acetamidothiazole-2-carboxylic acid have been nitrated and brominated and the results obtained have been presented. The significance of the results is discussed in the next part.

REFERENCES

1. Babo and Prijs .. *Helv. Chim. Acta*, 1950, **33**, 306.
2. Ochiai .. *J. Pharm. Soc. Japan*, 1938, **58**, 1040; *C.A.*, 1939, **33**, 3791.
3. Nagasawa .. *Ibid.*, 1940, **60**, 231, 433; *C.A.*, 1941, **35**, 458.
4. Prijs, Osterberg and Erlenmeyer *Helv. Chim. Acta*, 1947, **30**, 2110.
5. Ganapathi and Venkataraman .. *Proc. Ind. Acad. Sci.*, 1945, **22A**, 371.
6. ———— .. Unpublished observation (Thesis of Mrs. Venkataraman).
7. Prijs, Mengisen, Fallab and Erlenmeyer .. *Helv. Chim. Acta*, 1952. **35**, 187.
8. Ganapathi and Venkataraman .. *Proc. Ind. Acad. Sci.*, 1945, **22A**, 347.

γ-SUBSTITUTION IN THE RESORCINOL NUCLEUS

Part XI. Friedel and Crafts Acylation of 4-Nitroresorcinol

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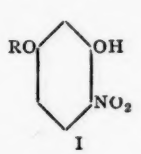
Parekh and Shah[1] observed that Pechmann condensation of 4-nitroresorcinol with ethyl acetoacetate furnishes 5-hydroxy-4-methyl-6-nitrocoumarin, the condensation occurring in the γ-position, rather than the more easily accessible β-position. Later, Chandrashekhar and Shah[2] made similar observation of γ-substitution during the Gattermann formylation of 4-nitroresorcinol.

In the present investigation 4-nitroresorcinol has been subjected to Friedel and Crafts acylations. 4-Nitroresorcinol (I, R = H), prepared by a slight modification of Kauffmann and Kugels[3] method, gave with acetic anhydride and anhydrous aluminium chloride in nitrobenzene, 2: 6-dihydroxy-3-nitroacetophenone (II, R = H), accompanied with a small amount of the known 5-nitro-resacetophenone (III). Both the products distilled with steam. The constitution of the former (II, R = H) was established by direct comparison with the product of nitration of 2: 6-dihydroxy-acetophenone (IV, R = H).

Friedel-Crafts acetylation of 4-nitroresorcinol-1-methyl ether (I, R = Me) gave the corresponding γ-substituted product: 2-hydroxy-3-nitro-6-methoxyacetophenone (II, R = Me). The same product was obtained on nitration of 2-hydroxy-6-methoxyacetophenone (IV, R = Me) and in small amounts on methylation of 2: 6-dihydroxy-3-nitroacetophenone (II, R = H), along with the dimethyl ether. It may be noted that the isomeric 2-hydroxy-5-nitro-6-methoxyacetophenone could not be isolated in any case.



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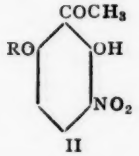

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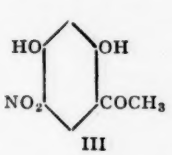

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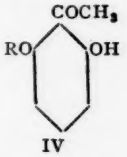

IV

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Further it is of interest to note that 2: 6-dihydroxy-3-nitroacetophenone and particularly its 6-methyl ether exhibit acidic properties; in aqueous sodium bicarbonate both easily dissolve with effervescence; the dimethyl ether gets easily demethylated to the 6-methyl ether (II, R = Me) with boiling alcoholic potassium hydroxide or cold concentrated sulphuric acid; while with boiling aqueous sodium hydroxide complete demethylation occurs yielding 2: 6-dihydroxy-3-nitroacetophenone (II, R = H). This may be due to the effect of two highly electrophilic substituents in the *ortho*-position to the hydroxyl, the effect being more pronounced in the case of the monomethyl ether (II, R = Me).

Similar Friedel-Crafts propionylation, butyrylation and benzoylation of 4-nitroresorcinol furnished 2: 6-dihydroxy-3-nitropropiophenone, 2: 6-dihydroxy-3-nitrobutyrophenone and 2: 6-dihydroxy-3-nitrobenzophenone respectively. The constitutions were established by direct comparison with products obtained on nitration of 2-propionyl-, 2-butyryl-, and 2-benzoylresorcinols.

The present observation further supports our earlier contention[1, 2] about the existence of chelation between OH and NO_2 in 4-nitroresorcinol which disturbs the equilibrium between the two resonating Kekule structures (A and B) and as a consequence the structure A predominates resulting in the superior reactivity of the γ-position.

EXPERIMENTAL

4-*Nitroresorcinol* (*I*, *R* = *H*)

It was prepared according to the method of Kauffmann and Kugel,[3] with slight modifications.

Resorcinol mono- and dibenzoates.—Benzoylation of resorcinol was carried out by the method of Barton, Linell and Senior.[4] Resorcinol (44·0 g.) was dissolved in a solution of sodium carbonate (88·0 g.) in water (1,300 c.c.) containing sodium hydrosulphite (5·0 g.). Benzoyl chloride (67·2 g.) was added dropwise with efficient stirring in 6–7 hours. The stirring was continued for further 2 hours. The crude mixture of resorcinol mono- and dibenzoates obtained was washed free from alkali and dried (78·0 g.).

Nitration of the mixture of resorcinol mono- and di-benzoates.—To a cooled solution (20°) of the crude mixture of resorcinol mono and dibenzoates (100 g.) in glacial acetic acid (1,000 c.c.), nitric acid (1·2 d.; 84 c.c.) was gradually added dropwise with mechanical stirring. The temperature slowly rose to 36–38°. It was left at room temperature for 4 hours,

diluted and the precipitate collected and washed several times with water. The crude mixture (104–105 g.) of 4- and 6-nitroresorcinol-3-benzoates and 4-nitroresorcinol dibenzoate thus obtained was directly subjected to hydrolysis.

4-*Nitroresorcinol.*—The crude mixture (100 g.) obtained above was kept overnight in sodium hydroxide solution (10%; 800 c.c.) and then heated on a steam-bath for 4-5 hours, when the whole substance went into solution. It was cooled, just acidified and filtered after cooling. The solution was extracted with ether, the ethereal layer was shaken with sodium bicarbonate solution to remove benzoic acid, washed with water, dried and ether removed. 4-Nitroresorcinol, obtained as a yellow powder, was crystallised from benzene in orange red prisms, m.p. 122° (22·0 g.). Kauffmann and Kugel[3] and Parekh and Shah[5] give the same melting point.

Friedel-Crafts Acetylation of 4-*Nitroresorcinol* (*I*, $R = H$): 2:6-*Dihydroxy*-3-*nitroacetophenone* (*II*, $R = H$) *and* 2:4-*Dihydroxy*-5-*nitroacetophenone* (*III*)

Dry 4-nitroresorcinol (6·4 g.) was added with cooling to a solution of anhydrous aluminium chloride (12·0 g.) in dry and distilled nitrobenzene (80 c.c.). To the cooled mixture acetic anhydride (4·0 c.c.) was cautiously added with occasional shaking and the reaction mixture kept overnight in a flask with calcium chloride-guard tube. Next day it was heated on a steam-bath for 4 hours, cooled and ice and dilute hydrochloric acid added. Nitrobenzene was removed by steam-distillation which was continued further when 2:6-dihydroxy-3-nitroacetophenone (II, R = H) being volatile in steam, passed off and condensed as fine yellow needles. Small quantity of 5-nitroresacetophenone (III) also passed over. The product was crystallised from excess of rectified spirit when 2:6-*dihydroxy*-3-*nitroacetophenone* (II, R = H) separated in fine pale yellow shining needles, m.p. 119° (3·0 g.) (Found: N, 7·1, $C_8H_7O_5N$ requires N, 7·1%). It gives blood red coloration with alcoholic ferric chloride and dissolves in aqueous sodium hydroxide giving orange red solution. It gives slight effervescence with sodium bicarbonate solution. It is soluble in alcohol and acetic acid and sparingly in benzene. *Oxime*, was crystallised from alcohol, fine pale yellow needles, m.p. 163° (Found: N, 13·9. $C_8H_8O_5N_2$ requires N, 14·1%). 2:4-*Dinitrophenylhydrazone*, was crystallised from glacial acetic acid, orange red prisms, m.p. 237° (Found: N, 18·2. $C_{14}H_{19}O_8N_5$ requires N, 18·6%).

The mother-liquor after removal of the above product (II, R = H) on concentration gave a product which after several crystallisations afforded 5-nitroresacetophenone (III) in thin colourless needles, m.p. and mixed

m.p. 142° (0·5 g.). Baker[6] gives the same melting point. It slowly distils over with steam as soft colourless needles and is difficultly soluble in sodium bicarbonate solution imparting yellow colour. *Oxime* was crystallised from alcohol in needles, m.p. 242° (Found: N, 14·0. $C_8H_8O_5N_2$ requires N, 14·1%). 2:4-*Dinitrophenylhydrazone* was crystallised from glacial acetic acid in yellow prisms, m.p. 268° (Found: N, 18·2. $C_{14}H_{11}O_8N_5$ requires N, 18·6%).

No diacetyl product could be isolated either from the steam distillate or from the mother-liquor after steam distillation, even on increasing the amount of aluminium chloride and acetic anhydride.

Nitration of 2:6-*Dihydroxyacetophenone* (*IV*, *R* = *H*). 2:6-*Dihydroxy*-3-*nitroacetophenone* (*II*, *R* = *H*) *and* 2:6-*Dihydroxy*-3:5-*dinitroacetophenone*

It was carried out according to the method of Naik and Jadhav,[7] with some modifications. Cooled nitric acid (0°) (d. 1·42; 5·0 c.c.) was added dropwise to a suspension of 2:6-dihydroxyacetophenone (2·0 g.) in ice-cold water (10 c.c.) with stirring. It was allowed to stand at room temperature (30°) for 5–6 minutes with occasional shaking. It was diluted and steam passed when 2:6-dihydroxy-3-nitroacetophenone (II, R = H) passed over, crystallised from alcohol (95%), m.p. and mixed m.p. 119° (0·7 g.). The residual solution after steam distillation gave 2:6-*dihydroxy*-3:5-*dinitroacetophenone*, crystallised from rectified spirit yellow flakes, m.p. 104° (1·0 g.) (Found: N, 11·9. $C_8H_6O_7N_2$ requires N, 11·6%). It gives red coloration with ferric chloride and dissolves in sodium bicarbonate solution with effervescence. *Oxime* was crystallised from alcohol in yellow needles, m.p. 221° (Found: N, 15·9, $C_8H_7O_7N_3$ requires N, 16·3%). 2:4-*Dinitrophenylhydrazone* was crystallised from glacial acetic acid, in fine red prisms, m.p. 211° (Found: N, 19·6. $C_{14}H_{10}O_{10}N_6$ requires N, 19·9%).

Friedel-Crafts Acetylation of 4-*Nitroresorcinol*-1-*methyl Ether* (*I*, *R* = *Me*), 2-*Hydroxy*-3-*nitro*-6-*methoxyacetophenone* (*II*, *R* = *Me*)

The monomethyl ether was prepared by refluxing 4-nitroresorcinol (3·2 g.), anhydrous potassium carbonate (5·0 g.), dimethyl sulphate (2·0 c.c.) in dry acetone (150 c.c.) for 24 hours. On working up as usual and crystallisation from alcohol (95%), it separated as thin yellow needles, m.p. 96° (1·8 g.). Weselsky and Benedict[8] give m.p. 95–96°.

4-Nitroresorcinol-1-methyl ether (I, R = Me) (1·7 g.), anhydrous aluminium chloride (3·0 g.) and acetic anhydride (1·0 c.c.) in dry nitrobenzene (25 c.c.) were heated for 4 hours at 135° protected from moisture. It was

cooled and ice and dilute hydrochloric acid added. Steam was passed when nitrobenzene and then the original compound passed over. The residual liquid after steam-distillation was extracted with ether. The extract was dried, ether removed and 2-*hydroxy*-3-*nitro*-6-*methoxyacetophenone* (*II*, *R* = *Me*) crystallised from alcohol (95%) in fine pale yellow needles, m.p. 102–103° (Found: N, 7·0. $C_9H_9O_5N$ requires N, 6·7%). It is sparingly soluble in water and gives a yellow solution. It gives a blood red coloration with alcoholic ferric chloride and dissolves in alkali to an orange solution. It gives effervescence with sodium bicarbonate solution. 2: 4-*Dinitrophenylhydrazone* was crystallised from glacial acetic acid in fine orange yellow needles, m.p. 201° (Found: N, 18·0. $C_{15}H_{13}O_8N_5$ requires N, 17·9%).

Nitration of 2-*Hydroxy*-6-*methoxyacetophenone* (*IV*, *R* = *Me*) : 2-*Hydroxy*-3-*nitro*-6-*methoxyacetophenone* (*II*, *R* = *Me*)

The mono-methyl ether could best be prepared by refluxing 2: 6-dihydroxyacetophenone (10·0 g.), anhydrous potassium carbonate (10·0 g.), dimethyl sulphate (6·0 c.c.) and dry acetone (400 c.c.) on a steam-bath for 24 hours. The reaction mixture was worked up as usual, taken up in dilute sodium hydroxide solution and dimethyl ether removed by washing with ether. The alkaline solution was acidified and distilled with steam when the mono-methyl ether passed over. It was crystallised from alcohol (95%) in fine light yellow needles, m.p. 60°. Gangal and Limaye[9] and Baker[10] give the same melting point.

The mono-methyl ether (IV, R = Me) (1·0 g.) in glacial acetic acid (10·0 c.c.) at 0° was dropwise treated with nitric acid (d. 1·42; 4·0 c.c.) with constant stirring. The mixture was kept at that temperature for 10 minutes and then diluted. It was steam-distilled to remove traces, if any, of the unreacted product. The residual liquid was extracted with ether, the ether extract dried and ether removed. The product obtained was crystallised from alcohol (95%) in thin yellow needles, m.p. 102–103°. Mixed melting point with the product obtained above was not lowered.

No trace of the isomeric 2-hydroxy-6-methoxy-5-nitroacetophenone could be isolated either from the steam-distillate or from the residual solution.

Methylation of 2: 6-*Dihydroxy*-3-*nitroacetophenone* (*II*, *R* = *H*) : 2: 6-*Dimethoxy*-3-*nitroacetophenone and* 2-*Hydroxy*-3-*nitro*-6-*methoxyacetophenone* (*II*, *R* = *Me*)

2: 6-Dihydroxy-3-nitroacetophenone (II, R = H) (5·0 g.), dimethyl sulphate (2·5 c.c.), anhydrous potassium carbonate (5·0 g.) and dry acetone 50 c.c.) were refluxed for 24 hours. The solution was filtered, acetone

removed and water and dilute sodium hydroxide solution added. It was extracted with ether, and the alkaline solution acidified and steam-distilled when the unreacted original substance passed over. The residual liquid on working up gave a small quantity of 2-hydroxy-6-methoxy-3-nitroacetophenone (II, R = Me), m.p. and mixed m.p. 102°.

The ether extract after drying and removal of ether gave 2: 6-dimethoxy-3-nitroacetophenone as an orange yellow oil. It did not give any coloration with aqueous alkali or alcoholic ferric chloride. The same oil was obtained on methylation of 2-hydroxy-6-methoxy-3-nitroacetophenone (II, R = Me) (2·1 g.) by refluxing with acetone (50 c.c.) and dimethyl sulphate (1·5 c.c.) in presence of anhydrous potassium carbonate (3·0 g.) for 12 hours. The dimethyl ether is insoluble in water, but miscible in alcohol and acetic acid. 2: 4-*Dinitrophenylhydrazone* was crystallised from glacial acetic acid in orange red prisms, m.p. 196° (Found: N, 17·5. $C_{16}H_{15}O_8N_5$ requires N, 17·3%).

Demethylation of 2: 6-*Dimethoxy*-3-*nitroacetophenone* : 2: 6-*Dihydroxy*-3-*nitroacetophenone* (*II, R = H*)

Dry dimethyl ether (2·25 g.) was added gradually to a cooled solution of anhydrous aluminium chloride (1·4 g.) in nitrobenzene (5·0 c.c.) when a vigorous reaction occurred. It was heated on a steam-bath for 2 hours, cooled and ice and dilute hydrochloric acid added. Steam was passed when nitrobenzene passed over followed by 2: 6-dihydroxy-3-nitroacetophenone, m.p. 118°. The residual solution after steam-distillation gave 2-hydroxy-6-methoxy-3-nitroacetophenone, m.p. 102°. No 2-hydroxy-6-methoxy-5-nitroacetophenone could be isolated.

Complete demethylation also occurred when the dimethyl ether (1·0 g.) was boiled with aqueous sodium hydroxide (10%; 20 c.c.) for an hour, giving 2: 6-dihydroxy-3-nitroacetophenone, m.p. 118°.

Partial Demethylation of 2: 6-*Dimethoxy*-3-*nitroacetophenone* : 2-*Hydroxy*-3-*nitro*-6-*methoxyacetophenone* (*II, R = Me*)

The dimethyl ether (1·0 g.), glacial acetic acid (15 c.c.) and concentrated hydrochloric acid (7·5 c.c.) were boiled for 3 hours. On working up the reaction mixture 2-hydroxy-3-nitro-6-methoxyacetophenone (II, R = Me), m.p. 102°, was obtained.

Similar partial demethylation also occurred when the dimethyl ether was refluxed with alcoholic potassium hydroxide (4%) (3 hours) or with concentrated hydrochloric acid (3 hours) or when kept at room temperature

(30°) with concentrated sulphuric acid (24 hours) furnishing 2-hydroxy-3-nitro-6-methoxyacetophenone (II, R = Me).

Friedel-Crafts Propionylation of 4-*Nitroresorcinol* : 2: 6-*Dihydroxy*-3-*nitropropiophenone*

Dry 4-nitroresorcinol (6·4 g.) was added to a cooled solution of anhydrous aluminium chloride (12·0 g.) in dry nitrobenzene (80 c.c.). Freshly distilled propionic anhydride (5·2 c.c.) was cautiously added with constant shaking. The reaction mixture was then heated in a steam-bath for 3 hours. It was cooled, ice and hydrochloric acid added and the contents steam-distilled. After passing over of nitrobenzene, the yellow 2: 6-*dihydroxy*-3-*nitropropiophenone* distilled over with steam. It was collected and crystallised from alcohol (95%) in thin yellow needles, m.p. 114–15° (Found: N, 7·0. $C_9H_9O_5N$ requires N, 6·7%). It gives blood red coloration with alcoholic ferric chloride and dissolves in aqueous alkali giving orange red solution. It slowly dissolves in sodium bicarbonate solution giving orange coloration.

Nitration of 2: 6-*Dihydroxypropiophenone* : 2:6 -*Dihydroxy*-3-*nitropropiophenone*

2: 6-Dihydroxypropiophenone (1·0 g.) was slowly added with constant shaking to nitric acid (d. 1·42; 5·0 c.c.) cooled to 0°. Soon the reaction mixture turned dark-red. It was kept at that temperature for 10 minutes, poured into ice-cold water and steam-distilled. The yellow needles which distilled over were collected and crystallised from alcohol in fine yellow needles, m.p. and mixed m.p. 114–15°.

Friedel-Crafts Butyrylation of 4-*Nitroresorcinol* : 2: 6-*Dihydroxy*-3-*nitrobutyrophenone*

To a well-cooled solution of anhydrous aluminium chloride (12·0 g.) in dry nitrobenzene (80 c.c.), dry 4-nitroresorcinol (6·4 g.) and butyric anhydride (7·2 c.c.) were successively added with constant shaking. The reaction mixture was heated on a steam-bath for 3 hours, cooled and ice and hydrochloric acid added. Nitrobenzene passed over with steam followed by 2: 6-*dihydroxy*-3-*nitrobutyrophenone*. It was collected and crystallised from alcohol (95%) in light yellow plates, m.p. 77–78° (Found: N, 6·5; $C_{10}H_{11}O_5N$ requires N, 6·2%). It gives blood red coloration with alcoholic ferric chloride and dissolves in aqueous alkali giving orange red solution. With aqueous sodium bicarbonate it gives a deep yellow solution.

Nitration of 2: 6-*Dihydroxybutyrophenone* : 2: 6-*Dihydroxy*-3-*nitrobutyrophenone*

Nitric acid (d. 1·42; 5 c.c.) was cooled to 0° and 2: 6-dihydroxybutyrophenone (1·0 g.) was slowly added with shaking. After keeping it at 0° for 10 minutes it was diluted with ice-cold water and the contents steam-distilled, 2: 6-dihydroxy-3-nitrobutyrophenone passed over and was collected and crystallised from alcohol (95%) in thin yellow plates, m.p. and mixed m.p. 78°.

Friedel-Crafts Benzoylation of 4-*Nitroresorcinol* : 2: 6-*Dihydroxy*-3-*nitrobenzophenone*

Dry 4-nitroresorcinol (6·4 g.), benzoic anhydride (14·0 g.), anhydrous aluminium chloride (12·0 g.) and dry nitrobenzene (80 c.c.) were heated on a steam-bath for 3 hours, and cooled. Ice and hydrochloric acid were added and nitrobenzene removed by steam-distillation. After cooling the residual liquid, the blackish mass was collected and washed with aqueous sodium bicarbonate to remove any benzoic acid. The residue was crystallised from 95% alcohol (charcoal) in thin yellow prisms, m.p. 158° (Found: N, 5·7. $C_{13}H_9O_5N$ requires N, 5·4%). It gives blood red coloration with alcoholic ferric chloride and dissolves in alkali imparting orange colour. It gives an orange solution with aqueous sodium bicarbonate.

Nitration of 2: 6-*Dihydroxybenzophenone* : 2: 6-*Dihydroxy*-3-*nitrobenzophenone*

2: 6-Dihydroxybenzophenone (1·0 g.) was added to nitric acid (d. 1·42; 5 c.c.) cooled to 0°. The reaction mixture turned red and some product separated. It was kept at 0° for 10 minutes and treated with cold water. The amber coloured precipitate was collected, washed and crystallised from (95%) alcohol (charcoal) in reddish yellow prisms, m.p. and mixed m.p. 157–158°.

SUMMARY

In extension of the previous work[1, 2] Friedel and Crafts acylation has been studied with 4-nitroresorcinol. 4-Nitroresorcinol on Friedel-Crafts acetylation furnished 2: 6-dihydroxy-3-nitroacetophenone along with small amounts of the known 5-nitroresacetophenone, substitution occurring mainly in the γ-position. 4-Nitroresorcinol-1-methyl ether similarly gave 2-hydroxy 3-nitro-6-methoxyacetophenone as the sole product. Similar γ-substitution was observed on Friedel-Crafts propionylation, butyrylation and benzoylation of 4-nitroresorcinol. The constitutions in all the cases have been established by comparing with the products of nitration of the corresponding

2-acylresorcinols. This observation furnishes further proof of existence of chelation in 4-nitroresorcinol resulting in the preferential substitution in the γ-position.

Some preliminary investigation on the Friedel-Crafts acylation was carried by Mr. (now Dr.) T. R. Chandrashekhar to whom the authors acknowledge their thanks. The authors are also grateful to Dr. S. M. Sethna for taking keen interest in the work.

References

1. Parekh and Shah .. *J. Indian Chem. Soc.*, 1942, **19**, 339.
2. Chandrashekhar and Shah .. *Proc. Indian Acad. Sci.*, 1949, **29A**, 227.
3. Kauffmann and Kugel .. *Ber.*, 1911, **44**, 753.
4. Barton, Linnell and Senior .. *J. Chem. Soc.*, **1945**, 436.
5. Parekh and Shah .. *J. Univ. Bombay*, 1943, **11** (V) A, 101.
6. Baker .. *J. Chem. Soc.*, **1934**, 1684.
7. Naik and Jadhav .. Unpublished.
8. Weselsky and Benedict .. *Monatsh.*, 1880, **1**, 892.
9. Gangal and Limaye .. *Rasayanam*, 1936, **1**, 65.
10. Baker .. *J. Chem. Soc.*, **1939**, 956.

CHROMONES

Part III. Kostanecki-Robinson Acylation of Some Ortho-Hydroxyacetophenones

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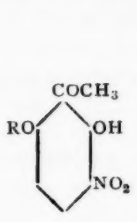
Since the work of Kostanecki and Rozycki[1] and its extension by Robinson and collaborators,[2] the reaction of *o*-hydroxy-acetophenones with the sodium salt of fatty acids and their anhydrides to form coumarins or chromones, generally known as Kostanecki-Robinson reaction, has been investigated by various workers.[3] This has been briefly reviewed by Sethna and Shah.[4] No work appears to have been done on the application of this reaction to hydroxy ketones having substituents like nitro-carbmethoxy, etc. In the present case Kostanecki-Robinson acetylation and benzoylation has been carried out with 2: 6-dihydroxy-3-nitroacetophenone, its monomethyl ether, 5-nitroresacetophenone and 2-hydroxy-6-methoxyacetophenone.

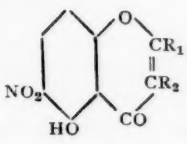
2: 6-Dihydroxy-3-nitroacetophenone (I, R = H) with acetic anhydride and sodium acetate at 150–55° gave two products, one having m.p. 161° (A) and another having m.p. 289° (B). The product, m.p. 289°, on boiling with aqueous solution of sodium carbonate gave the product, m.p. 161°. This product A on hydrolysis gave 4-nitroresorcinol (III). Coloration with alkali and ferric chloride indicated free hydroxyl groups in both the products. The following six products could be expected to be formed: 5-hydroxy-2-methyl-6-nitrochromone (II, R_1 = Me, R_2 = H), 5-hydroxy-2-methyl-3-acetyl-6-nitrochromone (II, R_1 = Me, R_2 = COMe), 5-hydroxy-2-methyl-8-nitrochromone (IV, R_1 = Me, R_2 = H), 5-hydroxy-2-methyl-3-acetyl-8-nitrochromone (IV, R_1 = Me, R_2 = COMe), 5-hydroxy-4-methyl-6-nitrocoumarin, and 5-hydroxy-4-methyl-8-nitrocoumarin. Out of these the last two, namely, 6-nitro-(m.p. 174–76°)[5] and 8-nitrocoumarins (m.p. 208–09°)[6] are known and have different melting points. Further, due to doubly chelated structure of 2: 6-dihydroxy-3-nitroacetophenone (as shown in V), it would be reasonable to expect that the hydroxy in 6-position and the acetyl in 1-position would take part in the reaction forming a 5-hydroxy-6-nitrochromone derivative. On this consideration the product A, m.p. 161°, has been assigned the structure, 5-hydroxy-2-methyl-6-nitrochromone (II, R_1 = Me, R_2 = H), and the product B, 5-hydroxy-2-methyl-3-acetyl-6-nitrochromone (II, R_1 = Me, R_2 = COMe).

On Kostanecki-Robinson reaction of 2:6-dihydroxy-3-nitro-acetophenone (I, R = H) with benzoic anhydride and sodium benzoate again two products were obtained, one having m.p. 209°, and the other m.p. 235–36°. The latter (m.p. 235–36°) on deacylation gave the former (m.p. 209°). On the same grounds as above, the former (m.p. 209°) has been assigned the structure 5-hydroxy-6-nitroflavone (II, R_1 = Ph, R_2 = H) and the latter (m.p. 235–36°) 5-hydroxy-3-benzoyl-6-nitroflavone (II, R_1 = Ph, R_2 = COPh).

Kostanecki-Robinson acetylation of 2-hydroxy-3-nitro-6-methoxyacetophenone (I, R = Me) furnished a product m.p. 216–217° which gave colora-



I



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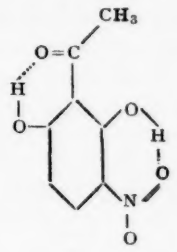

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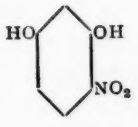

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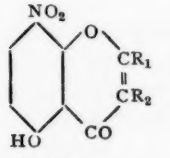

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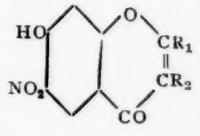

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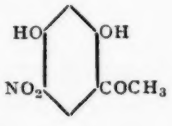

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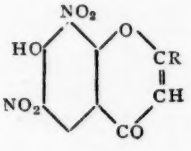
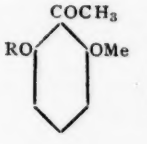
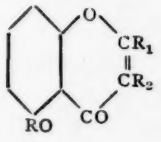


VII



IX



X

tion with alcoholic ferric chloride and had obviously a free hydroxyl group. Out of the six compounds likely to be formed with a free hydroxyl group which are listed above, it could not be any of the 6-nitrochromone derivatives (already described), nor could it be 5-hydroxy-4-methyl-6-nitrocoumarin[5] which has m.p. 174–76°, or 5-hydroxy-4-methyl-8-nitrocoumarin[6] because it gave coloration with alcoholic ferric chloride. Apparently it was 5-hydroxy-2-methyl-8-nitrochromone (IV, R_1 = Me, R_2 = H). It was also

obtained on nitration of 5-hydroxy-2-methylchromone (X, $R = R_2 = H$, $R_1 = Me$).[1]

There are several instances recorded in literature where demethylation occurs during this reaction.[8] However, it may be noted that all these cases are of Kostanecki-Robinson benzoylation and the present one appears to be the first instance where demethylation has taken place during acetylation. Another interesting point is that the demethylation has obviously occurred after the chromone formation as otherwise 5-hydroxy-2-methyl-6-nitrochromone would have formed (*v. supra*).

5-Nitroresacetophenone (VI) on Kostanecki-Robinson acetylation gave 7-hydroxy-2-methyl-3 acetyl-6-nitrochromone (VII, $R_1 = Me$, $R_2 = COMe$) which deacetylated to 7-hydroxy-2-methyl-6-nitrochromone (VII, $R_1 = Me$, $R_2 = H$). The latter on nitration gave the known 7-hydroxy-6: 8-dinitrochromone (VIII, $R = Me$).[9]

Similar Kostanecki-Robinson benzoylation of 5-nitroresacetophenone (VI) furnished 7-hydroxy-3-benzoyl-6-nitroflavone (VII, $R_1 = Ph$, $R_2 = COPh$) from which on debenzoylation 7-hydroxy-6-nitroflavone (VII, $R_1 = Ph$, $R_2 = H$) was obtained. This was nitrated to the known 7-hydroxy-6: 8-dinitroflavone (VIII, $R = Ph$).[9]

2-Hydroxy-6-methoxyacetophenone (IX, $R = H$) on Kostanecki-Robinson acetylation gave 5-methoxy-2-methyl-3-acetylchromone (X, $R = R_1 = Me$, $R_2 = COMe$) along with 2-acetoxy-6-methoxyacetophenone (IX, $R = COMe$). The above chromone on demethylation gave 5-hydroxy-2-methyl-3-acetylchromone (X, $R = H$, $R_1 = Me$, $R_2 = COMe$). Attempts at deacetylation however resulted in hydrolysis to 2-hydroxy-6-methoxyacetophenone (IX, $R = H$) showing very labile nature of the heterocyclic ring.

On similar Kostanecki-Robinson benzoylation of the same acetophenone (IX, $R = H$), 5-methoxy-3-benzoylflavone (X, $R = Me$, $R_1 = Ph$, $R_2 = COPh$) along with 5-benzoyloxy-3-benzoylflavone (X, $R = R_2 = COPh$, $R_1 = Ph$) was formed. The methoxyflavone on demethylation gave 5-hydroxy-3-benzoylflavone (X, $R = H$, $R_1 = Ph$, $R_2 = COPh$) and on debenzoylation furnished 5-hydroxyflavone (X, $R = R_2 = H$, $R_1 = Ph$), demethylation occurring simultaneously.

Attempts were made to carry out Kostanecki-Robinson acetylation and benzoylation on 3-nitroresacetophenone. However, only blackish products were obtained from which no pure crystallisable substance could be isolated.

Experimental

Kostanecki-Robinson Acetylation of 2:6-*Dihydroxy*-3-*nitroacetophenone* (*I*, $R = H$) : 5-*Hydroxy*-2-*methyl*-6-*nitrochromone* (*II*, $R_1 = Me$, $R_2 = H$) *and* 5-*Hydroxy*-2-*methyl*-3-*acetyl*-6-*nitrochromone* (*II*, $R_1 = Me$, $R_2 = COMe$)

2:6-Dihydroxy-3-nitroacetophenone[10] (6·0 g.) was heated with freshly fused powdered sodium acetate (5·0 g.), acetic anhydride (25 c.c.) and pyridine (5–6 drops) at 150–55° for 7 hours. The contents of the flask were poured in water containing little hydrochloric acid. The pasty mass obtained solidified on keeping and was collected, washed with water and dried. It was extracted with hot absolute alcohol (200 c.c.). The alcoholic solution was filtered hot. The filtrate on removal of alcohol gave pasty yellow product which was crystallised from acetic acid when fine pale yellow needles of 5-*hydroxy*-2-*methyl*-6-*nitrochromone* (*II*, $R_1 = Me$, $R_2 = H$), m.p. 161°, separated (1·2 g.) (Found: C, 54·6; H, 3·2; N, 6·7. $C_{10}H_7O_5N$ requires C, 54·4; H, 3·2; N, 6·3%). It gives blood-red coloration with alcoholic ferric chloride. It turns aqueous sodium hydroxide solution yellow and insoluble orange-yellow sodium salt separates out. Attempts to prepare its acetyl derivative met with failures.

The blackish residue, insoluble in alcohol, was refluxed with excess of acetic acid (charcoal) for about 2 hours, and filtered. The dark filtrate was further refluxed with more charcoal for half an hour, when a pale yellow solution was obtained. On concentration crystals of 5-*hydroxy*-2-*methyl*-3-*acetyl*-6-*nitrochromone* (*II*, $R_1 = Me$, $R_2 = COMe$) separated, which were recrystallised from acetic acid, in fine pale yellow needles, m.p. 289° (2·2 g.) (Found: C, 54·5; H, 3·3; N, 5·7. $C_{12}H_9O_6N$ requires C, 54·7; H, 3·4; N, 5·3%).

Deacetylation of 5-*Hydroxy*-2-*methyl*-3-*acetyl*-6-*nitrochromone* (*II*, $R_1 = Me$, $R_2 = COMe$) : 5-*Hydroxy*-2-*methyl*-6-*nitrochromone* (*II*, $R_1 = Me$, $R_2 = H$).

The 3-acetylnitrochromone (0·5 g.) was boiled with sodium carbonate solution (5%; 100 c.c.) for 3 hours. Some sodium salt separated out which did not go in solution even after long refluxing or with more of sodium carbonate solution. It was filtered hot. The insoluble sodium salt gave on acidification the unreacted original compound, m.p. 286°. The filtrate on acidification gave 5-hydroxy-2-methyl-6-nitrochromone (II, $R_1 = Me$, $R_2 = H$) crystallised from acetic acid, m.p. and mixed m.p. 161°.

Hydrolysis of 5-*Hydroxy*-2-*methyl*-6-*nitrochromone* (*II*, $R_1 = Me$, $R_2 = H$) : 4-*Nitroresorcinol* (*III*)

The chromone (0·5 g.) was boiled with sodium carbonate solution (10%; 20 c.c.) for 2 hours, when it dissolved giving an orange red solution.

It was cooled, acidified and extracted with ether. The extract was dried and ether removed when 4-nitroresorcinol,[10] m.p. and mixed m.p. 122°, was obtained.

Kostanecki-Robinson Benzoylation of 2: 6-*Dihydroxy*-3-*nitroacetophenone* (*I*, $R = H$): 5-*Hydroxy*-6-*nitroflavone* (*II*, $R_1 = Ph$, $R_2 = H$) *and* 5-*Hydroxy*-3-*benzoyl*-6-*nitroflavone* (*II*, $R_1 = Ph$, $R_2 = COPh$)

2: 6-Dihydroxy-3-nitroacetophenone (6·0 g.), freshly fused powdered sodium benzoate (8·5 g.), benzoic anhydride (30 g.) and pyridine (1·0 c.c.) were heated at 150–60° for 9 hours. The mixture on cooling solidified to a brown mass which was washed several times with hot water containing little hydrochloric acid to remove benzoic acid. The residual solid was collected, ground with sodium bicarbonate solution and then filtered and washed with water and dried. It was refluxed with absolute alcohol for 20 minutes and filtered hot. The filtrate on removal of alcohol gave 5-*Hydroxy*-6-*nitroflavone* (*II*, $R_1 = Ph$, $R_2 = H$) which was crystallised from acetic acid in fine yellow shining needles, m.p. 209° (1·8 g.) (Found: C, 64·0; H, 3·3; N, 5·1. $C_{15}H_9O_5N$ requires C, 63·7; H, 3·2; N, 5·2%). It gives blood-red coloration with alcoholic ferric chloride. With sodium hydroxide solution the insoluble yellow sodium salt separates out and the solution turns orange. Its acetyl derivative could not be prepared.

The alcohol-insoluble residue was refluxed with excess of acetic acid (charcoal) for about 2 hours and filtered. The filtrate gave, on cooling, yellow thick needles of 5-*hydroxy*-3-*benzoyl*-6-*nitroflavone* (*II*, $R_1 = Ph$, $R_2 = COPh$) (3·5 g.) recrystallised from acetic acid, m.p. 235–36° (Found: C, 68·6; H, 3·4; N, 4·0. $C_{22}H_{13}O_6N$ requires C, 68·2; H, 3·2; N, 3·6%). It gives blood-red coloration with alcoholic ferric chloride and turns sodium hydroxide solution yellow while the insoluble sodium salt separates.

Debenzoylation of 5-*Hydroxy*-3-*benzoyl*-6-*nitroflavone* (*II*, $R_1 = Ph$, $R_2 = COPh$): 5-*Hydroxy*-6-*nitroflavone* (*II*, $R_1 = Ph$, $R_2 = H$)

The 3-benzoylflavone (1·0 g.) was refluxed with alcoholic potassium hydroxide (5·0%; 100 c.c.) on a steam-bath for 3 hours. Some of it separated out as sodium salt which did not dissolve till the end. The solution was filtered hot. The insoluble sodium salt on acidification gave the original compound, m.p. 234°. The filtrate on removal of alcohol and acidification gave 5-hydroxy-6-nitroflavone (II, $R_1 = Ph$, $R_2 = H$) crystallised from acetic acid, m.p. and mixed m.p. 208°.

Kostanecki-Robinson Acetylation of 2-*Hydroxy*-3-*nitro*-6-*methoxy-acetophenone* (*I*, *R*=*Me*) : 5-*Hydroxy*-2-*methyl*-8-*nitrochromone* (*IV*, R_1=*Me*, R_2=*H*)

2-Hydroxy-3-nitro-6-methoxyacetophenone[10] (4·0 g.), fused sodium acetate (3·0 g.) and acetic anhydride (12 c.c.) with pyridine (5-6 drops) were heated at 155–60° for 7 hours. The dark solid obtained on pouring in dilute hydrochloric acid was collected, dried and refluxed with absolute alcohol (80 c.c.) on a steam-bath and filtered hot. The filtrate on removal of alcohol gave a dark yellow paste. It was crystallised from glacial acetic acid (charcoal) in thin light brown flakes, m.p. 216–17°. It gave red coloration with alcoholic ferric chloride, and formed insoluble sodium salt with aqueous sodium hydroxide. It did not depress the melting point of 5-hydroxy-2-methyl-8-nitrochromone (IV, R_1 = Me, R_2 = H) prepared by nitration of 5-hydroxy-2-methylchromone (X, R = R_2 = H, R_1 = Me).[7]

Kostanecki-Robinson Acetylation of 2 : 4-*Dihydroxy*-5-*nitroacetophenone* (*VI*) : 7-*Hydroxy*-2-*methyl*-3-*acetyl*-6-*nitrochromone* (*VII*), R_1=*Me*, R_2=*COMe*)

5-Nitroresacetophenone (VI) was prepared by slightly modifying the method of Baker.[11] Resacetophenone (20 g.) in glacial acetic acid (100 c.c.) at 0° was dropwise treated with nitric acid (d. 1·42; 100 c.c.). It was left at room temperature (30°) for 10–15 minutes. When brown fumes just started to evolve, it was diluted with iced water. The brown product was crystallised from glacial acetic acid (charcoal), when 5-nitroresacetophenone separated in thick amber-coloured needles, m.p. 142° (14 g.). Baker[11] gives the same melting point. It slowly distils over with steam as a white flocculent product.

5-Nitroresacetophenone (10·0 g.) was heated with fused sodium acetate (8·0 g.) and acetic anhydride (40 c.c.) at 150–55° for 7 hours. The blackish product obtained was washed with water and then with some boiling alcohol. The black residue was repeatedly refluxed with acetic acid and the extract was concentrated. On cooling soft yellow needles of 7-*hydroxy*-2-*methyl*-3-*acetyl*-6-*nitrochromone* (VII, R_1 = *Me*, R_2 = *COMe*), m.p. 264° were obtained (yield 4·2 g.) (Found: C, 54·2; H, 3·3; N, 5·8. $C_{12}H_9O_6N$ requires C, 54·7; H, 3·4; N, 5·3%). It gave faint brownish coloration with alcoholic ferric chloride solution and sodium hydroxide solution turns yellow, the sodium salt separating out.

Deacetylation of 7-*Hydroxy*-3-*methyl*-2-*acetyl*-6-*nitrochromone* (*VII*), R_1 =*Me*, R_2=*COMe*) : 7-*Hydroxy*-2-*methyl*-6-*nitrochromone* (*VII*, R_1=*Me*, R_2=*H*)

7-Hydroxy-2-methyl-3-acetyl-6-nitrochromone (2·0 g.) was refluxed with sodium carbonate solution (5%; 50 c.c.) for 2 hours. The deep red solution

obtained was cooled and acidified. *7-Hydroxy-2-methyl-6-nitrochromone* (*VII*, $R_1 = Me$, $R_2 = H$) obtained as yellow precipitate was collected, washed and crystallised from acetic acid (yield, 0·8 g.). It did not melt below 305° but melted on a spatula leaving no residue. (Found: C, 54·5; H, 3·2; N, 6·4. $C_{10}H_7O_5N$ requires C, 54·4; H, 3·2; N, 6·3%.) The product gave faint brownish coloration with alcoholic ferric chloride. It turns sodium hydroxide solution yellow and the sodium salt separates out.

7-Hydroxy-2-methyl-6-nitrochromone (1·0 g.) when nitrated with a cooled mixture of nitric acid (d. 1·42; 5·0 c.c.) and concentrated sulphuric acid (5·0 c.c.) at room temperature (*c.* 30°) for 24 hours, gave 7-hydroxy-2-methyl-6: 8-dinitrochromone (VIII, R = Me),[9] m.p. and mixed m.p. 233°.

Kostanecki-Robinson Benzoylation of 2; 4-*Dihydroxy*-5-*nitroacetophenone* (*VI*): 7-*Hydroxy*-3-*benzoyl*-6-*nitroflavone* (*VII*, $R_1 = Ph$, $R_2 = COPh$)

5-Nitroresacetophenone (6·0 g.), freshly fused sodium benzoate (8·5 g.) and benzoic anhydride (30·0 g.) were heated in an oil-bath at 185–90° for 8 hours. The crude product obtained on working up the reaction mixture was refluxed with acetic acid (charcoal). The yellow solution thus obtained was concentrated when *7-hydroxy*-3-*benzoyl*-6-*nitroflavone* (*VII*, $R_1 = Ph$, $R_2 = COPh$) separated in pale yellow granules. It was recrystallised from acetic acid, in faint yellow needles, m.p. 272–73° (yield, 2·8 g.) (Found: C, 68·6; H, 3·4; N, 4·0. $C_{22}H_{13}O_6N$ requires C, 68·2; H, 3·4; N, 3·6%). It gives light brown coloration with alcoholic ferric chloride. With sodium hydroxide solution a pale yellow solution is obtained, while the sodium salt separates out.

Debenzoylation of 7-*hydroxy*-3-*benzoyl*-6-*nitroflavone* (*VII*, $R_1 = Ph$, $R_2 = COPh$): 7-*Hydroxy*-6-*nitroflavone* (*VII*, $R_1 = Ph$, $R_2 = H$)

7-Hydroxy-3-benzoyl-6-nitroflavone (2·0 g.) was refluxed with alcoholic potassium hydroxide solution (5%; 40 c.c.) on a steam-bath for an hour. The substance first went into a dark red solution and then yellow flocculent precipitate separated out. Most of the alcohol was removed, the residue diluted with water and then acidified. The substance that separated was collected, washed and crystallised from alcohol (95%) in brown rhombic needles, m.p. 232–33° (Found: C, 64·0; H, 3·4; N, 5·1. $C_{15}H_9O_5N$ requires C, 63·6; H, 3·2; N, 4·9%). It gives brown coloration with alcoholic ferric chloride. With alkali, the insoluble sodium salt separates out, the solution turning yellow.

7-Hydroxy-6-nitroflavone (1·0 g.) was nitrated with nitric acid (d. 1·42; 5·0 c.c.) in glacial acetic acid (7·0 c.c.) by heating on a steam-bath for 20

minutes. 7-Hydroxy-6: 8-dinitroflavone (VIII, R = Ph)[9] separated as yellow needles m.p. and mixed m.p. 288–89°.

Kostanecki-Robinson Acetylation of 2-*Hydroxy*-6-*methoxyacetophenone* (*IX, R = H*): 5-*Methoxy*-2-*methyl*-3-*acetylchromone* (*X, R = R*$_1$ = *Me, R*$_2$ = *COMe*) *and* 2-*Acetoxy*-6-*methoxyacetophenone* (*IX, R = COMe*)

2-Hydroxy-6-methoxyacetophenone[10] (5·0 g.), fused sodium acetate (5·0 g.) and acetic anhydride (15·0 c.c.) were heated at 160–65° for 7 hours. The reaction mixture on dilution gave a white flocculent precipitate and a brownish paste which solidified to granular crystals. The flocculent product found to be 5-methoxy-2-methyl-3-acetylchromone (X, R = R$_1$ = Me, R$_2$ = COMe) was carefully collected, washed and crystallised from alcohol in thin colourless needles, m.p. 147° (yield, 1·4 g.) (Found: C, 67·4; H, 5·2. Calc. for $C_{13}H_{12}O_4$: C, 67·2; H, 5·2%). Limaye and Kelkar[13] give m.p. 149–51°. It did not give any coloration with alcoholic ferric chloride, nor did it dissolve in alkali.

The methoxychromone (0·5 g.) on demethylation with hydriodic acid (3·0 c.c.) and acetic anhydride (5·0 c.c.) at 140° for 2 hours gave 5-hydroxy-2-methyl-3-acetylchromone (X, R = H, R$_1$ = Me, R$_2$ = COMe), m.p. and mixed m.p. 121°. Attempts at deacetylation of the chromone (2·0 g.) by refluxing with sodium carbonate solution (2%; 30 c.c.) for 1½ hours resulted only in hydrolysis to 2-hydroxy-6-methoxyacetophenone (IX, R = H), m.p. 60°.

The granular solid on crystallisation from alcohol gave colourless crystals, m.p. 80° and was found to be 2-*methoxy*-6-*acetoxyacetophenone* (*IX, R = COMe*) as it did not depress the m.p. of the product prepared by acetylation of the monomethyl ether (1·0 g.) with acetic anhydride (5·0 c.c.) and pyridine (0·5 c.c.) at room temperature (*c.* 30°) for 4 hours (Found: C, 63·3; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·7%).

Kostanecki-Robinson Benzoylation of 2-*Hydroxy*-6-*methoxyacetophenone* (*IX, R = H*): 5-*Benzoyloxy*-3-*benzoylflavone* (*X, R = R*$_2$ = *COPh, R*$_1$ = *Ph*) *and* 5-*methoxy*-3-*benzoylflavone* (*X, R = Me, R*$_1$ = *Ph, R*$_2$ = *COPh*)

The monomethyl ether (5·0 g.), fused sodium benzoate (7·5 g.) and benzoic anhydride (30·0 g.) were heated in an oil-bath at 185–90° for 8 hours. The product obtained on working up the reaction mixture as usual, was refluxed with alcohol. The light brown granular product which did not dissolve was collected from the hot mixture and crystallised from acetic acid (charcoal) in thick pale yellow prisms; the m.p. and mixed m.p. wi h 5-benzoyloxy-3-benzoylflavone (X, R = R$_2$ = COPh, R$_1$ = Ph)[14] was 234°.

The alcoholic extract was refluxed with activated charcoal for about 1½ hours, filtered and the filtrate concentrated when *5-methoxy-3-benzoylflavone* (*X*, *R* = *Me*, R_1 = *Ph*, R_2 = *COPh*) was obtained in fine shining yellow needles, m.p. 182° (Found: C, 77·2; H, 4·2. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%). It did not give any coloration with ferric chloride and was insoluble in alkali.

The methoxy flavone (0·5 g.) on demethylation by heating with hydroiodic acid (3·0 c.c.) in acetic anhydride (4·0 c.c.) at 140° for 2 hours gave 5-hydroxy-3-benzoylflavone (X, R = H, R_1 = Ph, R_2 = COPh)[15], m.p. and mixed m.p. 173°. Debenzoylation of the methoxyflavone (2·0 g.) by refluxing with alcoholic potassium hydroxide (4%; 30 c.c.) for half an hour gave 5-hydroxyflavone (X, R = R_2 = H, R_1 = Ph), m.p. and mixed m.p. 155°, demethylation occurring simultaneously.

SUMMARY

Kostanecki-Robinson reaction has been studied with various *ortho*-hydroxyacetophenones. 2:6-Dihydroxy-3-nitroacetophenone on Kostanecki-Robinson acetylation gave 5-hydroxy-2-methyl-6-nitrochromone and 5-hydroxy-2-methyl-3-acetyl-6-nitrochromone, and on benzoylation gave 5-hydroxy-6-nitroflavone and 5-hydroxy-3-benzoyl-6-nitroflavone. 2-Hydroxy-3-nitro-6-methoxyacetophenone, however, surprisingly, gave 5-hydroxy-2-methyl-8-nitrochromone, demethylation occurring after the chromone formation. 5-Nitroresacetophenone on similar acetylation and benzoylation gave 7-hydroxy-2-methyl-3-acetyl-6-nitrochromone and 7-hydroxy-3-benzoyl-6-nitroflavone respectively which were deacylated to the corresponding simple chromone and flavone derivatives. 2-Hydroxy-6-methoxyacetophenone on Kostanecki-Robinson acetylation gave 5-methoxy-2-methyl-3-acetyl-chromone along with 2-acetoxy-6-methoxyacetophenone, while on benzoylation a mixture of 5-methoxy- and 5-benzoyloxy-3-benzoylflavones was obtained.

The authors are grateful to Dr. R. C. Shah and Dr. S. M. Sethna for their keen interest in the work.

REFERENCES

1. Kostanecki and Rozycki .. *Ber.*, 1901, **34**, 102.
2. Robinson *et al.* .. *J. Chem. Soc.*, 1924, 2192; 1925, 1973, 1981; 1926, 2344; 1929, 61; 1932, 925.
3. Robertson *et al.* .. *Ibid.*, 1931, 1245. 1255, 1877.
   Heilbron *et al.* .. *Ibid.*, 1933, 1263; 1934, 1311, 1581; 1936, 295.
   Venkataraman *et al.* .. *Ibid.*, 1931, 1165, 2376, 2591; 1932, 918, 930; 1933, 616, 1459.
4. Sethna and Shah .. *J. Ind. Chem. Soc.*, 1940, **17**, 239.

5.	Parekh and Shah	.. *J. Ind. Chem. Soc.*, 1942, **19**, 339.
6.	————	.. *Ibid.*, 1942, **19**, 335.
7.	Naik, Mehta, Thakor, Jadhav and Shah	Under publication.
8.	Wessely and Moser	.. *Monatsh.*, 1930, **56**, 97; 1932, **60**, 26.
	Baker	.. *J. Chem. Soc.*, 1939, 956.
9.	Rao and Seshadri	.. *Proc. Ind. Acad. Sci.*, 1945, **22A**, 383.
10.	Mehta, Jadhav and Shah	.. *Ibid.*, 1949, **29A**, 314.
11.	Naik, Thakor and Shah	.. Under publication.
12.	Baker	.. *J. Chem. Soc.*, 1934, 1684.
13.	Limaye and Kelkar	.. *Rasayanam*, 1936, **1**, 24.
14.	————	.. *J. Ind. Chem. Soc.*, 1935, **12**, 788.
15.	Trivedi, Sethna and Shah	.. *Ibid.*, 1943, **20**, 171.
16.	Baker	.. *J. Chem. Soc.*, 1934, 1953.
17.	Sugasawa	.. *Ibid.*, 1934, 1483.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXXI. A Synthesis of 7-Hydroxy-chromeno-(3′: 4′: 2: 3)-chromone

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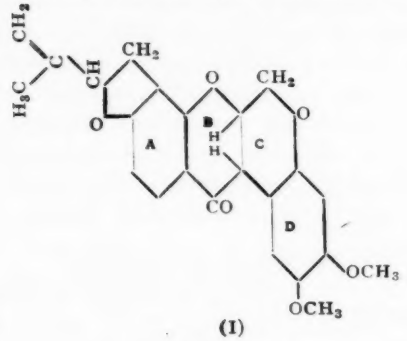
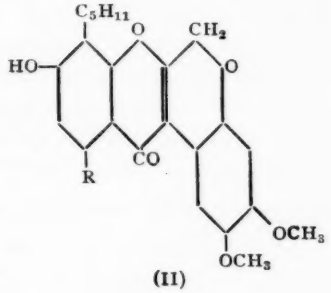
Received February 16, 1953

ONE of the most important natural insecticides of plant origin is rotenone (I). A number of related compounds also occur in nature and all these contain a chromanone unit (rings A and B) and a chroman unit (rings C and D). These are therefore known as chromano-chromanones.

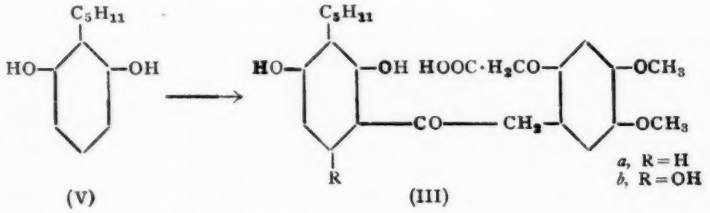
The structure of rotenone has been based mainly on a number of degradation studies. The most important synthetic support for this structure is the synthesis of dehydro-tetrahydro-rotenone (II *a*) by Robertson.[1] It had been found earlier[2] that when this compound is heated with alcoholic alkali in presence of zinc dust, it gives rise to tetrahydro-derrisic acid (III *a*) which could be reconverted into (II *a*) by heating with sodium acetate and acetic anhydride.[3] This conversion was considered by Robertson to take place through the hypothetical stages (IV *a*) and (IV *b*). He prepared (III *a*) starting with tetrahydro-tubanol (V).



(I)

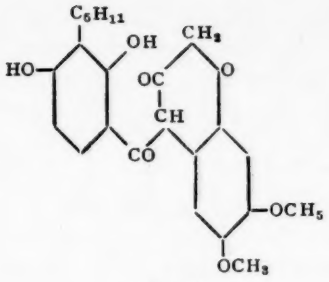


(II)

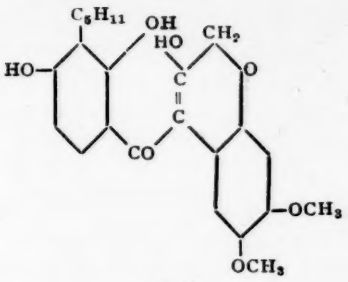


(V) (III)

a, R = H
b, R = OH

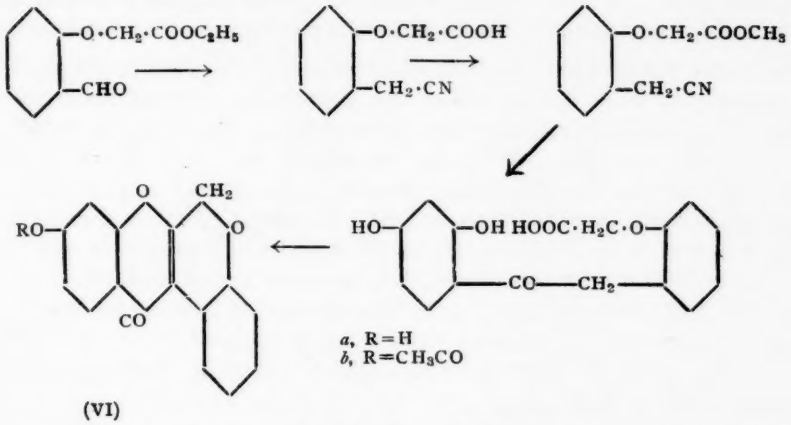


(IV *a*)



(IV *b*)

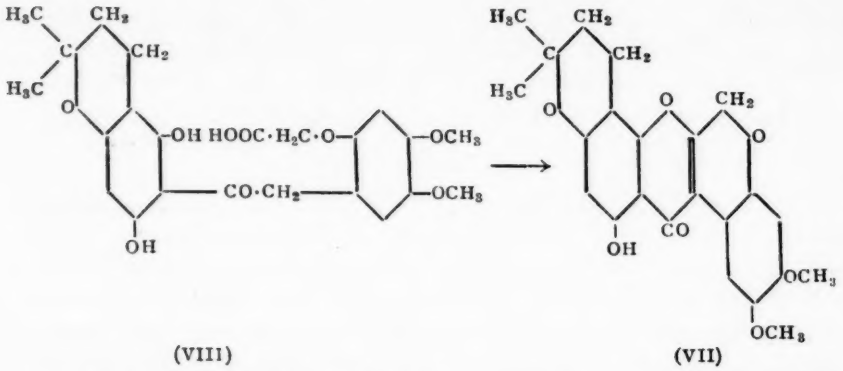
The above synthesis represented the first method of preparation of chromeno-chromones. Following it, simpler chromeno-chromones were also synthesised by Robertson.[4] The simplest of these, 7-acetoxy-chromeno-(3′: 4′: 2: 3)-chromone (VI *b*) was obtained starting from salicyl aldehyde and passing through the steps indicated below.



a, R = H
b, R = CH_3CO

(VI)

Although this method is of wide applicability, it cannot be used for the unambiguous synthesis of 8-alkyl-5: 7-dihydroxy-chromeno-(3: 4′: 2: 3)-chromones of dehydro-tetrahydro-sumatrol type. The trihydroxy acid (III *b*) can give rise to two products, *viz.*, the 6-alkyl and 8-alkyl chromeno-chromones. Kenny, Robertson and George[5] stated that only an 8-alkyl derivative is formed in such a case and they reported the conversion of tetrahydro-sumatrolic acid (III *b*) into dehydro-tetrahydro-sumatrol (II *b*). Similarly dehydro-dihydro-toxicarol (VII) and not the isomeric compound is said to be formed by treating dihydro-toxicarolic acid (VIII) with sodium acetate and acetic anhydride.[6]



(VIII) (VII)

In the above conversions, both the chromene and chromone units are simultaneously formed. Attempts have been made by Richards, Robertson and Ward[7] to build up first a chromene unit and then a chromone unit, evidently with a view to more firmly establish the presence of such structures in rotenone and its analogues, but these experiments have not been successful.

Although the presence of chromanone and chroman units in rotenone and related compounds is indicated by the degradation reactions, no degradation products containing either the chromanone or chroman unit intact have so far been obtained. As already mentioned, the conversion of acids of tetrahydro-derrisic type (III *a*) into chromeno-chromones postulates some intermediates which have not been isolated. It seemed therefore necessary to evolve a new route for the synthesis of chromeno-chromones in which these ring systems are formed step by step by unambiguous methods. The ambiguities that exist in the original synthesis of 5: 7-dihydroxy-8-alkyl chromeno-chromones have already been pointed out and hence the new procedure should be free from this defect. Such a synthetic route has now been successfully explored.

For this purpose, a method based on the possible biogenetic evolution of the chromano-chromanone ring system would appear to have the best chance of success. No suggestion seems to have been so far made on its biogenesis. The occurrence of the following compounds suggests the stages of a reasonable scheme.

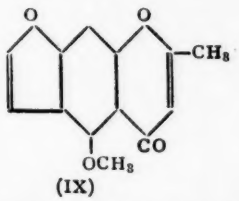
(1) Padmakastein, a simple representative of isoflavanones, was recently discovered by Narasimhachari and Seshadri.[8] It gives the Durham test characteristic of rotenone and related compounds.

(2) Though the synthetic work described in the earlier parts of this series[9, 10] relating to isogenistein and 8-methyl isogenistein do not support

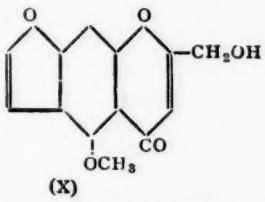
the constitutions given to certain components of soya beans, the isolation of *o*-hydroxy phenyl acetic acid as one of the products of their degradation would indicate that 2′-hydroxy isoflavone structures are present in them. There is no doubt that pterocarpin and homopterocarpin[12] are 2′-hydroxy isoflavan derivatives in which this hydroxyl group is engaged in ether formation.

(3) Although no 2-methyl isoflavone is known so far to occur in nature, the simpler chromones contain a number of representatives having a methyl group in the 2-position. Four such occur in *Eugenia caryophyllata*.[13] Further examples are provided by kellin, visnagin (IX) and chellol (X) isolated from *Ammi visnaga*.[14] Among these, chellol has a hydroxymethyl group in place of the methyl group. Consequently, the postulation of 2-methyl isoflavanones as intermediates in the evolution of rotenone and related compounds has some basis.

(4) There is particular interest in the occurrence of visnagin (IX) and chellol (X) in the same plant *Ammi visnaga*. These two compounds are closely related and visnagin may be considered to arise from chellol by reduction or conversely, chellol can result by oxidation of visnagin.



(IX)



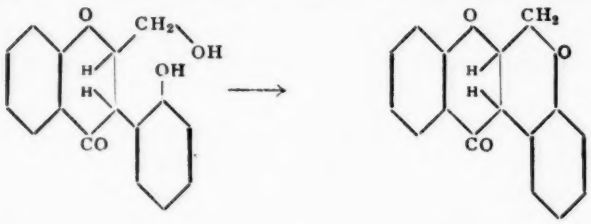
(X)

Such examples of C-methyl and C-carbinol derivatives occurring together are found elsewhere also. Among the anthraquinones, physcion and teloschistin are found to occur together in the lichen *Teloschistes flavicans*.[15] A similar pair is chrysophanol and aloe-emodin, isolated from *Cascara sagrada*.[16]

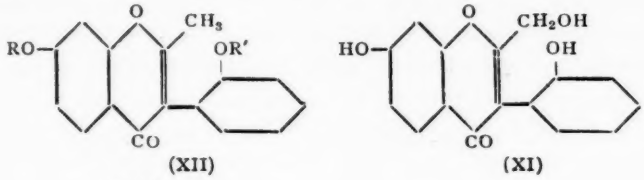
In some Indian strains of the lichen *Parmelia tinctorum*, the depside atranorin is found to occur along with the depsidone, nor-stictic acid[17] or salazinic acid.[18] These three compounds are closely related and represent different stages of oxidation. The second and third have a methyl and a carbinol group respectively in the corresponding positions. As indicated earlier,[19] it is quite possible that the carbinol group represents an earlier stage and the methyl group arises as the result of reduction.

Taking all the abovementioned points into consideration, it is reasonable to conclude that the chroman ring of chromano-chromanones arises by

the elimination of water involving the 2′-hydroxyl group and the carbinol present in the 2-position of an isoflavanone system as indicated below.



As the first step in the adoption of the above biogenetic scheme in the laboratory, the synthesis of the chromeno-chromone (VI *a*) has now been attempted. The main stage is the preparation of a 2′-hydroxy isoflavone with a carbinol group in the 2-position (XI). For this purpose, the related 2-methyl isoflavone (XII *a*) is prepared as the necessary intermediate.



(XII) (XI)

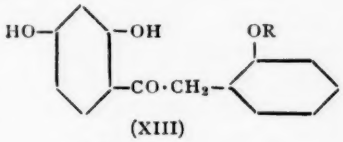
a, R = R′ = H
b, R = R′ = CH_3CO
c, R = H, R′ = CH_3
d, R = R′ = CH_3
e, R = CH_3, R′ = H

It is well known that a methyl group situated in the 2-position of chromones and isoflavones is highly reactive and yield 2-styryl derivatives on condensation with aromatic aldehydes.[20, 21] In a recent publication[22] was described the successful substitution of a hydrogen atom of the 2-methyl group of isoflavones with a bromine atom using N-bromo succinimide as reagent. This reaction has now been applied to the case of the diacetoxy methyl isoflavone (XII *b*) and the product subsequently converted into 7-hydroxy-chromeno-(3′ : 4′ : 2 : 3)-chromone (VI *a*).

The required isoflavone (XII *a*) could presumably be obtained from 2 : 4 : 2′-trihydroxy phenyl benzyl ketone (XIII *a*) and therefore the preparation of this ketone was attempted by the Hoesch condensation of *o*-hydroxy phenyl acetonitrile[4] with resorcinol. The ketimine hydrochloride was formed in a good yield. On hydrolysis with water, a product melting at 146–48° and having a negative ferric reaction in alcoholic solution was

obtained. However it gave a deep pink colour with ferric chloride in aqueous solution and it was identified as *o*-hydroxy phenyl acetic acid. No trace of the ketone could be detected. Complete fission seems to be taking place during hydrolysis. Similar results have been obtained by using C-methyl phloroglucinol in place of resorcinol in the above Hoesch condensation and it appears that 2′-hydroxy phenyl benzyl ketone cannot be prepared by the Hoesch reactions.

The required 2-methyl-7: 2′-diacetoxy isoflavone (XII *b*) has been prepared by an alternative route. Condensation of *o*-methoxy phenyl acetonitrile[9] with resorcinol gives 2: 4-dihydroxy-2′-methoxy phenyl benzyl ketone (XIII *b*). On heating with acetic anhydride and sodium acetate, the dihydroxy ketone (XIII *b*) yields 2-methyl-7-acetoxy-2′-methoxy isoflavone, which on hydrolysis gives rise to the 7-hydroxy compound (XII *c*). By demethylation with aluminium chloride in benzene solution, it is converted into 2-methyl-7: 2′-dihydroxy isoflavone (XII *a*). This does not give any colour with alcoholic ferric chloride. Acetylation of the product yields the required diacetate (XII *b*).

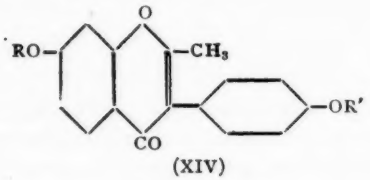


(XIII)

a, R=H
b, R=CH_3

On heating 2-methyl-7: 2′-diacetoxy isoflavone with one mole of N-bromo succinimide in carbon tetrachloride solution in presence of benzoyl peroxide, succinimide slowly crystallises out. The mother-liquors yield 2-bromomethyl-7: 2′-diacetoxy isoflavone. When this compound is heated with alcoholic hydrochloric acid for 2 hours, hydrolysis of the acetyl groups takes place and simultaneously the bromine atom is replaced by the hydroxyl group, giving rise to (XI). Attempts at closing the chromone ring by heating (XI) with acetic anhydride were not successful. However, it is found that when an acetone solution of this compound is heated with anhydrous potassium carbonate, one mole of water is removed and 7-hydroxy-chromeno-(3′: 4′: 2: 3)-chromone (VI *a*) is obtained. This product, on acetylation, yields the acetate (VI *b*) melting at 182–83°. Robertson,[4] who obtained it by a different route discussed earlier, reported the melting point to be 178°. Hence these two substances may be considered to be identical. The present method therefore constitutes an unambiguous synthesis of a chromeno-chromone and confirms the validity of the earlier synthesis.[4]

Incidentally, methylation experiments have been carried out with 2-methyl-7: 2′-dihydroxy isoflavone (XII *a*). On heating with excess of methyl iodide and potassium carbonate in acetone solution, this compound gives rise to a product soluble in dilute sodium hydroxide. It is different from 2-methyl-7: 2′-dimethoxy isoflavone (XII *d*) prepared by methylation of 2-methyl-7-hydroxy-2′-methoxy isoflavone (XII *c*). Its composition and properties show that it is a monomethyl ether but it is not identical with the 2′-monomethyl ether (XII *c*) and therefore it should be 2-methyl-7-methoxy-2′-hydroxy isoflavone (XII *e*). Confirmation is provided by the acetate of this compound being also different from 2-methyl-7-acetoxy-2′-methoxy isoflavone. Under the same conditions of methylation, 2-methyl-7: 4′-dihydroxy isoflavone (XIV *a*) yields predominantly the dimethyl ether (XIV *b*) along with a small quantity of the 7-methyl ether (XIV *c*) an authentic sample of which is obtained conveniently by the partial demethylation[23] of (XIV *b*). There is thus clear indication that the 2′-hydroxy group is somewhat resistant to methylation. The absence of any ferric reaction in the case of 2-methyl-7: 2′-dihydroxy isoflavone (XII *a*) shows that there is no chelate bond between the carbonyl group and the 2′-hydroxyl group and therefore the resistance of the 2′-hydroxyl group to methylation should be due to other factors, probably steric. In the above methylation, besides the alkali-soluble monomethyl ether (XII *e*), a small amount of alkali insoluble dimethyl ether (XII *d*) is also formed and this shows that the resistance to methylation is not very strong.



(XIV)

a, R=R′=H
b, R=R′=CH_3
c, R=CH_3, R′=H

EXPERIMENTAL

Hoesch condensation using o-hydroxy phenyl acetonitrile

To a solution of *o*-hydroxy phenyl acetonitrile (8 g.) and dry resorcinol (8 g.) in dry ether (250 c.c.) was added fused zinc chloride (2 g.). The mixture was cooled to 0° and dry hydrogen chloride passed through it for 4 hours. After 16 hours, the ketimine hydrochloride was separated from the ether layer, washed with dry ether twice and then heated with water (150 c.c.) for

2 hours. On cooling to 0°, a small amount of dark solid separated. This was filtered off and the filtrate concentrated to 25 c.c. on a steam-bath and cooled. Colourless crystals separated. When recrystallised from water, the product was obtained as colourless rectangular prisms melting at 146–48°. A mixed melting point with an authentic sample of *o*-hydroxy phenyl acetic acid was not depressed. Yield, 5·5 g. It was soluble in aqueous sodium bicarbonate and gave a deep pink colour with ferric chloride in aqueous solution.

2: 4-*Dihydroxy-2'-methoxy phenyl benzyl ketone* (*XIII* b)

Resorcinol (12 g.) and *o*-methoxy phenyl acetonitrile[9] (13 g.) were dissolved in dry ether (150 c.c.) and zinc chloride (2 g.) was added. Dry hydrogen chloride was passed for 5 hours through the mixture, cooled in an ice-bath. It was left overnight in the ice-chest. The ether layer was decanted off from the heavy dark red oily ketimine hydrochloride which was then washed with dry ether and heated with water (150 c.c.) for 2 hours in a water-bath. The sticky solid that came out on leaving overnight in the refrigerator was separated by decanting off the aqueous layer. It was then macerated with cold alcohol (10 c.c.) when a colourless solid separated. It was filtered and washed with a small amount of ice-cold alcohol. When crystallised from the same solvent, 2: 4-dihydroxy-2'-methoxy phenyl benzyl ketone was obtained as colourless square plates and prisms melting at 159–60°. Yield, 6·3 g. It gave a reddish pink colour with alcoholic ferric chloride. It dissolved in dilute sodium carbonate to give a colourless solution (Found: C, 70·1; H, 5·5; $C_5H_{14}O_4$ requires C, 69·8; H, 5·4%).

2-*Methyl-7-acetoxy-2'-methoxy isoflavone*

The above ketone (4 g.) was heated with fused sodium acetate (8 g.) and acetic anhydride (50 c.c.) for 12 hours at 170–80° and the solution poured on crushed ice. After 4 hours, most of the acetic acid was carefully neutralised with dilute sodium hydroxide. On leaving overnight, a sticky solid separated. The aqueous layer was decanted off and residue crystallised from alcohol twice. 2-Methyl-7-acetoxy-2'-methoxy isoflavone separated as long colourless rectangular rods and prisms melting at 113–15°. Yield, 2·3 g. It was easily soluble in hot alcohol (Found: C, 70·4; H, 5·3; $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9%).

2-*Methyl-7-hydroxy-2'-methoxy isoflavone* (*XII* c)

The above acetate (2·1 g.) was dissolved in alcohol (100 c.c.) and treated with concentrated sulphuric acid (4·5 c.c.). The solution was refluxed for 2 hours. On cooling the hydroxy compound crystallised out. Yield,

1·65 g. When recrystallised from alcohol twice, it was obtained in the form of very thick colourless rectangular prisms melting at 225–27°. It did not give any colour with alcoholic ferric chloride and was soluble in dilute sodium carbonate (Found: C, 72·1; H, 5·0; $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%).

2-Methyl-7: 2′-dimethoxy isoflavone (*XII* d)

The above hydroxy isoflavone (0·5 g.) in acetone (50 c.c.) was heated with dimethyl sulphate (0·2 c.c.) and potassium carbonate (2 g.) for 4 hours. The acetone solution was separated from the potassium salts by filtration and then distilled. The residue was treated with water. After keeping overnight, the solid was filtered and crystallised from alcohol. 2-Methyl-7: 2′-dimethoxy isoflavone came out as long colourless rectangular rods melting at 138–39°. Yield, 0·4 g. (Found: C, 72·9; H, 5·4; $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). It was insoluble in dilute sodium hydroxide and was easily soluble in alcohol, ethyl acetate and acetone.

2-Methyl-7: 2′-dihydroxy isoflavone (*XII* a)

2-Methyl-7-hydroxy-2′-methoxy isoflavone (1 g.) was suspended in dry benzene (50 c.c.) and treated with anhydrous aluminium chloride (3 g.) and the mixture refluxed for 2 hours. The dark semi-solid residue left on distillation of the solvent was treated with ice and hydrochloric acid (6 c.c.). After 2 hours, the colourless solid was filtered and purified by dissolution in aqueous sodium carbonate (10%). 2-Methyl-7: 2′-dihydroxy isoflavone crystallised from alcohol as colourless rhombohedral prisms melting at 241–43° (decomp.). Yield, 0·6 g. It did not give any colour with alcoholic ferric chloride (Found: C, 72·0; H, 4·7; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

In later experiments, it was found that this dihydroxy isoflavone could be directly and conveniently obtained from 2-methyl-7-acetoxy-2′-methoxy isoflavone which is easily soluble in benzene unlike 2-methyl-7-hydroxy-2′-methoxy isoflavone. In this case, deacetylation and demethylation take place simultaneously by the treatment described in the above para.

2-Methyl-7: 2′-diacetoxy isoflavone (*XII* b)

The above dihydroxy compound (1·6 g.) was heated with acetic anhydride (20 c.c.) and pyridine (3 c.c.) for 2 hours at 150° and the solution poured on crushed ice. The colourless precipitate was filtered after 15 hours and crystallised from alcohol when the diacetate separated as colourless tablets melting at 117–19°. Yield, 1·35 g. It was easily soluble in alcohol (Found: C, 68·4; H, 4·4; $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%).

2-Bromomethyl-7: 2'-diacetoxy isoflavone

2-Methyl-7: 2'-diacetoxy isoflavone (1·15 g.) was dissolved in carbon tetrachloride (40 c.c.). Freshly prepared and dried N-bromo succinimide (0·58 g., 1 mole) and benzoyl peroxide (0·05 g.) were added and the mixture refluxed on a water-bath. The heavy crystals of N-bromo succinimide dissolved slowly and after 15 hours, when all the N-bromo succinimide had dissolved, the clear solution was cooled. Succinimide crystallised out and the crystals floated on the solution. The crystals were filtered off and washed with a small quantity of carbon tetrachloride. These melted at 124–25° and a mixed melting point with an authentic sample of succinimide was not depressed. The filtrate was distilled and the residual oil washed twice with hot water. The residue was then extracted with ether and the ether solution dried over anhydrous sodium sulphate. The residue left on distillation of ether did not solidify on cooling to 0° and could not be obtained as a solid. Qualitative tests proved the presence of bromine in the substance. It was directly hydrolysed as described below.

Hydrolysis to 2-hydroxymethyl-7: 2'-dihydroxy isoflavone (XI)

The above acetate (1·2 g.) was dissolved in alcohol (25 c.c.) and mixed with concentrated hydrochloric acid (25 c.c.). The mixture was refluxed on a water-bath for 2 hours. The solution was cooled, diluted with water (75 c.c.) and left overnight in the refrigerator. The precipitated solid was collected and crystallised from alcohol twice when 2-hydroxymethyl-7: 2'-dihydroxy isoflavone (XI) separated as very thick colourless tablets melting at 219–22° (decomp.). Yield, 0·5 g. (Found: C, 67·3; H, 4·6; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%). It was sparingly soluble in alcohol. It gave no test for the presence of bromine. The easy hydrolysis of the bromide under the above conditions is significant. The same effect is produced even when the compound is boiled for 5 minutes with a mixture of alcohol (1 part) and conc. hydrochloric acid (1 part).

7-Hydroxy-chromeno-(3': 4': 2: 3)-chromone (VI a)

The above compound (0·3 g.) was dissolved in dry acetone (100 c.c.) and the solution refluxed for 10 hours with anhydrous potassium carbonate (3 g.). Acetone was then distilled off and water was added to the residue, when a clear solution was obtained. It was acidified with hydrochloric acid and the precipitated solid was collected and crystallised twice from alcohol, when it came out as pale yellow needles and rectangular rods melting at 240–42° (decomp.). Yield, 0·17 g. It was easily soluble in alcohol (Found: C, 72·3; H, 4·1; $C_{16}H_{10}O_4$ requires C, 72·2; H, 3·8%).

The acetate (VI *b*) was prepared by acetylation of the above hydroxy compound with acetic anhydride and pyridine. It was crystallised twice from alcohol and then from a mixture of alcohol and acetic acid, when it separated as colourless plates and needles melting at 182–83°. It was sparingly soluble in alcohol and benzene and easily in acetic acid. Robertson[4] who obtained it by a different route gives the m.p. as 178° (Found: C, 69·6; H, 4·2; $C_{18}H_{12}O_5$ requires C, 70·1; H, 3·9%).

2-Methyl-7-methoxy-2′-hydroxy isoflavone (*XII* e)

2-Methyl-7: 2′-dihydroxy isoflavone (0·4 g.) was dissolved in dry acetone (150 c.c.) and the solution refluxed with methyl iodide (3 c.c.) and anhydrous potassium carbonate (2 g.) for 3 hours. The potassium salts were filtered off and washed with acetone. The liquid residue left on distilling off acetone was treated with ether (100 c.c.) and aqueous sodium hydroxide (30 c.c. of 10%). The alkaline layer was drawn off and the ether solution extracted with small volumes of aqueous sodium hydroxide two more times. The combined alkaline solution was cooled to 0° and acidified. The colourless precipitate was filtered and crystallised from alcohol. 2-Methyl-7-methoxy-2′-hydroxy isoflavone separated as colourless rectangular plates and prisms melting at 238–40°. It was sparingly soluble in alcohol. It was insoluble in dilute sodium carbonate. Yield, 0·29 g. (Found: C, 72·0; H, 5·4; $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%).

The ether solution left after extraction with alkali was washed with water and then distilled. The residue crystallised from alcohol as colourless rectangular rods melting at 138–39°. A mixed melting point with 2-methyl-7: 2′-dimethoxy isoflavone (XII *d*) described earlier was not depressed. Yield, 25 mg.

2-Methyl-7-methoxy-2′-acetoxy isoflavone

2-Methyl-7-methoxy-2′-hydroxy isoflavone (0·25 g.) was acetylated with acetic anhydride (4 c.c.) and pyridine (5 drops) at 140° during 2 hours. The acetate crystallised from alcohol as colourless stout rectangular prisms melting at 197–99°. It was very sparingly soluble in alcohol (Found: C, 70·5; H, 5·3; $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9%).

2-Methyl-7-hydroxy-4′-methoxy isoflavone

This compound was prepared earlier by Baker *et al.*[20] by the hydrolysis of its acetate with alcoholic potash. The hydrolysis has now been carried out using alcoholic sulphuric acid.

2-Methyl-7-acetoxy-4′-methoxy isoflavone (2·4 g.) was dissolved in alcohol (200 c.c.), concentrated sulphuric acid (8 c.c.) was added and the

mixture refluxed in a water-bath for 2 hours. Water (200 c.c.) was added and the alcohol removed by distillation. The precipitate was collected and crystallised from alcohol. 2-Methyl-7-hydroxy-4′-methoxy isoflavone was obtained as colourless stout prisms melting at 280–81°. Yield, 2·0 g.

2-*Methyl*-7 : 4′-*dimethoxy isoflavone* (*XIV* b)

2-Methyl-7-hydroxy-4′-methoxy isoflavone was prepared by Baker *et al.*[20] by the hydrolysis of its acetate with alcoholic potash. This hydrolysis has now been carried out more conveniently using alcoholic sulphuric acid, the procedure being the same as already described for the preparation of (XII *c*). For the methylation of this hydroxy compound, methyl sulphate and potassium hydroxide were employed in the past.[20] It is more convenient to use methyl sulphate and potassium carbonate in dry acetone solution. The product (XIV *b*) melts at 170–71°.

2-*Methyl*-7-*methoxy*-4′-*hydroxy isoflavone* (*XIV* c)

To a solution of the above compound (1 g.) in acetic anhydride (10 c.c.), hydriodic acid (15 c.c., d. 1·7) was added and the mixture heated in an oil-bath at 115–20° for 30 minutes and then cooled and diluted with aqueous sodium bisulphite (80 c.c.). The precipitate was collected and treated with aqueous sodium carbonate (10%). The undissolved residue was filtered and macerated with aqueous sodium hydroxide (5%) repeatedly. Almost the whole of it dissolved. The filtrate on acidification yielded 2-methyl-7-methoxy-4′-hydroxy isoflavone (0·5 g.). It came out as colourless rectangular prisms from alcohol and melted at 242–44° (Found: C, 72·5; H, 5·4; $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%).

The acetate crystallised from alcohol as colourless needles and plates melting at 160–62° (Found: C, 69·9; H, 5·3; $C_{19}H_{16}O_5$ requires C, 70·4; H, 5·0%).

2-*Methyl*-7 : 4′-*dihydroxy isoflavone* (*XIV* a)

To a solution of 2-methyl-7-acetoxy-4′-methoxy isoflavone (1·7 g.) in hot benzene (50 c.c.), anhydrous aluminium chloride (6 g.) was added and the mixture refluxed for 2 hours. Benzene was then distilled off and ice and hydrochloric acid (10 c.c.) were added. After 2 hours, the precipitate was collected and purified by dissolution in aqueous sodium carbonate. When crystallised from alcohol, 2-methyl-7 : 4′-dihydroxy isoflavone was obtained as colourless thin rectangular plates melting at 315–18° (decomp.). Yield, 1·1 g. It was easily soluble in hot alcohol. It did not give any colour with ferric chloride in alcoholic solution. (Found: C, 71·8; H, 5·0; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

The diacetate separated from alcohol as colourless thick rectangular prisms melting at 192–93° (Found: C, 68·4; H, 4·8; $C_{20}H_{16}O_6$ requires C, 68·0; H, 4·5%).

Methylation of 2-methyl-7: 4′-dihydroxy isoflavone

A solution of the above dihydroxy compound (0·4 g.) in acetone (150 c.c.) was treated with methyl iodide (3 c.c.) and potassium carbonate (3 g.). The mixture was refluxed for 3 hours. The potassium salts were filtered off and washed with acetone. The solvent was distilled off from the filtrate and water was added to the residue. The precipitate was collected and treated with aqueous sodium hydroxide (5%). The insoluble portion was filtered, washed with water and crystallised from alcohol. It separated as flat prisms melting at 170–71°, alone or when mixed with an authentic sample of 2-methyl-7: 4′-dimethoxy isoflavone (XIV *b*). Yield 0·18 g.

The sodium hydroxide solution was acidified and the precipitate collected and crystallised from alcohol. It was obtained as colourless rectangular prisms melting at 242–44°. A mixed melting point with an authentic sample of 2-methyl-7-methoxy-4′-hydroxy isoflavone (XIV *c*) was not depressed. Yield 25 mg.

SUMMARY

The evolution of the chromano-chromanone unit present in rotenone and related compounds is of much interest. From a consideration of a number of structures occurring in nature, it is suggested that 2-hydroxymethyl-2′-hydroxy isoflavanone or its equivalent is an intermediate and it undergoes ring closure by dehydration.

Based on this hypothesis, a synthesis of 7-hydroxy-chromeno-(3′: 4′; 2: 3)-chromone has now been achieved. 2-Methyl-7: 2′-diacetoxy isoflavone is converted into a 2-bromomethyl compound by treatment with N-bromo succinimide. On hydrolysis and treatment with potassium carbonate in acetone, it yields 7-hydroxy-chromeno-(3′: 4′: 2: 3)-chromone.

Though attempts to prepare the required diacetoxy isoflavone directly from 2: 4: 2′-trihydroxy phenyl benzyl ketone have not been successful, it could be obtained starting from 2: 4-dihydroxy-2′-methoxy phenyl benzyl ketone and treatment of the intermediate 2-methyl-7-acetoxy-2′-methoxy isoflavone with aluminium chloride in benzene solution, followed by acetylation.

Methylation of 2-methyl-7: 2′-dihydroxy isoflavone with excess of methyl iodide gives rise to the 7-methyl ether, indicating the existence of a considerable difference in the reactivities of the 7 and 2′-hydroxyl groups. The

negative ferric reaction of these 2′-hydroxy compounds shows absence of chelation.

References

1. Roberts7n .. *J.C.S.*, 1933, 1163.
2. LaForge and Smith .. *J.A.C.S.*, 1930, 1094 and 3603.
3. ——— and Haller .. *Ibid.*, 1932, 810.
4. Robertson .. *J.C.S.*, 1933, 489.
5. Kenny, Robertson and George.. *Ibid.*, 1939, 1601.
6. George and Robertson .. *Ibid.*, 1937, 1535.
7. Richards, Robertson and Ward *Ibid.*, 1948, 1610.
8. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1952, **35A**, 202.
9. Seshadri and Varadarajan .. *Ibid.*, 1953, **37A**, 514.
10. ———— .. *Ibid.*, 1953, **37A**, 526.
11. Okano and Beppu .. *J. Agri. Chem. Soc., Japan*, 1939, **15**, 645.
12. McGookin, Robertson and Whalley *J.C.S.*, 1940, 787.
13. Schmid *et al.* .. *Helv. Chim. Acta*, 1948, **31**, 1603; 1949, **32**, 843 and 1358; 1950, **33**, 17o1.
14. Fantl and Salem .. *Biochem. Ztschr.*, 1930, **226**, 166.
    Spath *et al.* .. *Ber.*, 1938, **71B**, 106; 1941, **74B**, 1492 and 1549.
15. Seshadri and Subramanian .. *Proc. Ind. Acad. Sci.*, 1949, **30A**, 67.
16. Lidder *et al.* .. *J. Amer. Pharm. Ass.*, 1942, **31**, 1616.
17. Seshadri and Subramanian .. *Proc. Ind. Acad. Sci.*, 1949, **30A**, 62.
18. Neelakantan, Seshadri and Subramanian *Jour. Sci. Ind. Res. India*, 1951, **10B**, 199.
19. Seshadri .. *Proc. Ind. Acad. Sci.*, 1944, **20A**, 1; 1949, **30A**, 331.
20. Baker, Robinson and Simpson .. *J.C.S.*, 1933, 274.
21. ———— .. *Ibid.*, 1937, 805.
22. Sehgal and Seshadri .. *Jour. Sci. Ind. Res. India*, 1953 (in press).
23. Aghoramurthy, Narasimhachari and Seshadri *Proc Ind. Acad. Sci.*, 1951, **33A**, 257.

A COMPOUND OF 2:6-DIMETHOXY QUINONE AND ACETONE

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In an earlier publication,[1] a brief study of the methylation of hydroxy quinones was made. It was noticed that even under mild conditions using methyl sulphate, potassium carbonate and acetone the quinones underwent reduction (by dismutation) and subsequent methylation giving rise to the methyl ethers of corresponding quinols. When 2:6-dimethoxy quinone (I) is used in these experiments the result is different and an unexpected new product is formed which has now been studied in detail. Instead of the usual dismutation and methylation leading to the expected tetramethoxy benzene, the product is found to have very different properties. It is a colourless substance melting at 158–59°, readily soluble in water and has a sweet taste. It gives no colour with ferric chloride solution. Analysis for carbon and hydrogen and molecular weight determination indicate that it has resulted simply by the addition of an acetone molecule with a molecule of 2:6-dimethoxy quinone. Later experiments have shown that it could be more conveniently obtained by heating a solution of the quinone in acetone in presence of anhydrous potassium carbonate or by adding absolute alcoholic potash to a suspension of the quinone in acetone. The product is unstable in presence of moisture; even when heated in benzene solution for a long time, or as solid at its melting point for a short time, it decomposes into the original quinone and acetone. This decomposition is much faster in alkaline solution but the resulting quinone undergoes further changes whereas the acetone can be recovered.

The new compound gives definite derivatives for the presence of an alcoholic hydroxyl group (acetylation and benzoylation) and for a carbonyl group (2:4-dinitro phenyl hydrazone and semi-carbazone). It also gives the iodoform reaction. It however does not undergo methylation. The analysis of these derivatives again supports the formula of the substance as an addition product. In suggesting a constitution for it, the following possibilities have to be considered:

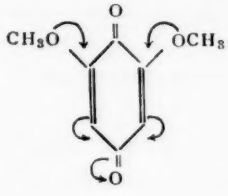
1:4-*Addition.*—This is quite common with *p*-benzoquinones giving rise to the corresponding quinol derivatives. But this characteristic quinone property is considerably affected by substitution.[2] 2:6-Dimethoxy quinone is known to be an extremely inert substance towards Thiele mixture and

hydrogen chloride. This inertness has been attributed[3] partly to the result of neutralisation of the 4-carbonyl group by both the methoxyls (formula I) diminishing unsaturation in the nuclear double bonds and making the katio-enoid system less reactive and partly to the steric effects. Hence an 1 : 4-addition in the present case will be improbable. In fact the properties of the addition compound are different from those of 2 : 6-dimethoxy quinol as are shown in the following table (Table I).

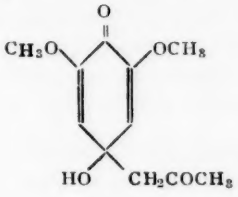
TABLE I

Properties studied	2 : 6-Dimethoxy quinol	2 : 6-Dimethoxy quinone-acetone compound
Solubility in water	.. Sparingly soluble	Readily soluble
Sodium hydroxide	.. Intense green solution	The initial colourless solution soon becomes rose red.
Conc. sulphuric acid	.. Deep red solution	Initial brown colour changes to bluish violet.
Methylation	.. Can be readily methylated	Cannot be methylated.
Bromine in chloroform	Gives the crystalline 2 : 6-dimethoxy-3 : 5-dibromo quinone	Gives a sticky semi-solid which could not be crystallised.

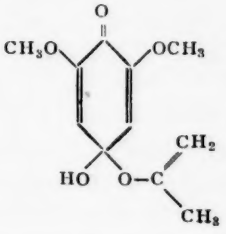
1 : 2-*Addition.*—For reasons given in the above para, the diminished activity of the double bond of the ring will lead to removal of conjugation or diminution of conjugation and consequently an increase in the carbonyl activity of the two C = O groups. The more active of the two will be the one in the 4-position since it is sterically free and will have a greater access of electrons for ready co-ordination with protons. Based on these considerations, the following formulæ could be suggested (II and III).



(I)



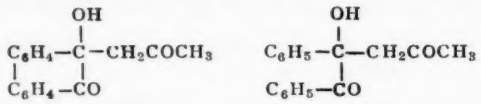
(II)



(III)

Formula II seems to explain satisfactorily all the properties and reactions of the compound. Particular mention may be made of the ready formation of the 2:4-dinitro phenyl hydrazone. This is readily soluble in aqueous alkali and can be recovered unchanged by acidifying the alkaline solution. The second alternative (III) would attribute the ketonic properties to the quinone carbonyl in position 1, and in analogous cases of pseudoquinols, the reaction with phenyl hydrazine is more complex and yields alkyl azo compounds.[4]

In this connection may be mentioned the earlier study of the addition products of phenanthrenequinone and acetone,[5] and benzil and acetone[6] by Japp and co-workers. Phenanthrenequinone reacts with acetone with or without sodium hydroxide as a condensing agent, giving a colourless addition product. The addition product is readily soluble in water and is readily decomposed on heating at its melting point or heating its solution in water, into acetone and phenanthrene quinone. Among the possible formulæ, they considered (IV) as the most probable. Similarly they represented the constitution of the product formed from benzil and acetone as (V).



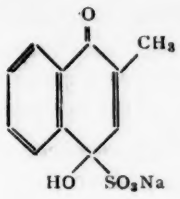
(IV) (V)

The above examples are different from 2:6-dimethoxy quinone in that the first is an orthoquinone and the second an α-diketone and they contain two similarly located carbonyl groups whereas in 2:6-dimethoxy quinone one carbonyl is different from the other. Hence the complications[5] observed in the behaviour of the orthoquinone and benzil are not noticed in the present case. Similar 1:2-addition has been proposed by Staudinger,[7] for the reaction between diphenyl keten and *p*-benzoquinone. Diphenyl keten reacts with *p*-benzoquinone in the cold giving compounds of the types (VI and VII). These compounds seem to have considerable stability and are decomposed only on very strong heating. More recently it has been noticed,[8] that *p*-benzoquinone combines with pyridine acetate and formate yielding addition products. It may also be mentioned here that 1:2-addition of sodium bisulphite is considered to take place with menadione to form the water-soluble addition product (VIII).[9]

Among simple *p*-benzoquinones, the combination with acetone seems to be peculiar to 2:6-dimethoxy quinone and obviously the enhanced carbonyl activity of one of the C = O group is necessary. Other quinones like *p*-benzoquinone, and 2:5-dimethoxy-*p*-benzoquinone do not react with

(VI)

(VII)



(VIII)

acetone under similar conditions. Methyl ethyl ketone is also found to form an addition product readily with 2: 6-dimethoxy quinone.

Experimental

2: 6-*Dimethoxy-p-benzoquinone*

For the preparation of this substance in a pure state, the procedure of Baker *et al.*[10] was followed with slight modifications intended to remove effectively the accompanying nitro compound. A typical experiment is described below.

A mixture of pyrogallol trimethyl ether (55 g.), alcohol (275 c.c.) and nitric acid (275 c.c.; d. 1·2) was warmed to 35° and allowed to stand until vigorous reaction set in; the temperature was then kept below 50° for ¼ hour. After 4 hours, the quinone was filtered, washed with water (300 c.c.) and then with benzene (200 c.c.). The residue was then almost pure quinone melting at 252–53°, and it was used directly for the experiments described in this paper.

The benzene washings were collected separately and distilled; the residue was filtered and washed with sodium hydroxide solution to remove any of the quinone present. It was then recrystallised from ethanol when it was obtained as colourless stout prisms melting at 109–10°. It was identical with 5-nitro pyrogallol trimethyl ether the m.p. of which however had been reported earlier as 100°.[11] (Found: C, 50·9; H, 5·2; $C_9H_{11}NO_5$ requires C, 50·7; H, 5·2%.) This compound is sparingly soluble in cold alcohol, but is very soluble in cold benzene and hence its removal is efficiently accomplished by washing the mixture with benzene.

Condensation of 2: 6-*dimethoxy quinone and acetone*

(i) *Using anhydrous potassium carbonate.*—A suspension of 2: 6-dimethoxy quinone (5 g.) and anhydrous potassium carbonate (5 g.) in dry acetone (100 c.c.) was refluxed for 6 hours. After half an hour the quinone

went into solution. The pale brown reaction mixture was filtered and the potassium salt was washed with hot dry acetone. The combined filtrate and washings were evaporated to dryness. The residue weighing 4 g. was crystallised from a mixture of dry acetone and dry ether. Colourless glistening plates of the addition product melting at 158–59° were obtained.

(ii) *Using alcoholic potassium hydroxide.*—To a suspension of 2:6-dimethoxy quinone (5 g.) in acetone (15 c.c.) was added dropwise absolute alcoholic potassium hydroxide (0·5 c.c.; 10%). The quinone immediately went into solution and the mixture turned deep brown. There was a slight increase in temperature. After 15 minutes the acetone was partially allowed to evaporate in the cold, and benzene (100 c.c.) was added. The brown solid so obtained was filtered, washed with benzene, and immediately recrystallised from acetone-ether mixture. Colourless crystals of the addition product were obtained melting at 158–59°. Yield, 4 g.

Properties of the addition compound

It is sparingly soluble in benzene and ether, but easily in acetone, alcohol and water. It has a mild sweet taste. It does not give any colour with ferric chloride solution. In 5% aqueous sodium hydroxide, the initial colourless solution soon changes to rose red. In concentrated sulphuric acid it forms a deep brown solution which on gentle warming changes into intense bluish violet colour. When an aqueous solution is heated it readily decomposes into acetone and 2:6-dimethoxy quinone. When heated above its melting point it is decomposed into original quinone and acetone. It also gives the iodoform reaction (Found: C, 58·4, 58·6; H, 5·7, 6·6; molecular weight: 216, 227 (depression of freezing point of water); $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%; and molecular weight, 226).

Acetate

The addition compound (1 g.) was acetylated by heating with acetic anhydride (5 c.c.) and sodium acetate (1 g.) at 140° for 1 hour. It was then treated with water and the resulting solid was recrystallised from methanol. The acetate came out as colourless needles melting at 127–28° (Found: C, 58·6; H, 6·4; $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0%).

Benzoate

The addition compound (1 g.) was dissolved in pyridine (15 c.c.) and benzoyl chloride (2 c.c.) was added. The resulting solution was kept at room temperature for 36 hours. It was then treated with water and extracted with ether. The ether solution was washed with ice-cold 2 N hydrochloric acid, then with saturated sodium bicarbonate solution and finally with water

and distilled. The resulting oily liquid was crystallised from petroleum ether when the benzoyl derivative was obtained as long rectangular prisms melting at 52–53°.

2:4-*Dinitro phenyl hydrazone*

An aqueous solution of the addition compound (1 g.) was treated with a solution of 2:4-dinitrophenyl hydrazine (1 g.) in 4 N hydrochloric acid (25 c.c.). The resulting yellow precipitate was filtered, washed with dilute hydrochloric acid, and water. On recrystallisation from ethyl acetate, it was obtained as bright orange needles melting at 214–15°. The 2:4-dinitro phenyl hydrazone is soluble in aqueous sodium hydroxide producing a deep green solution, and is reprecipitated on the addition of acid (Found: C, 50·6; H, 4·8; $C_{17}H_{18}O_8N_4$ requires, C, 50·2; H, 4·4%).

Semicarbazone

The addition compound (1 g.) was dissolved in water and treated with semicarbazide hydrochloride (1 g.) and sodium acetate (1 g.) heated to boiling, cooled and the resulting solid was recrystallised from alcohol. The semicarbazone was obtained as colourless prisms melting at 200–01°.

Acetone estimation

When an aqueous solution of the addition compound was treated with ammonia and iodine in potassium iodide, a yellow solid was obtained. The identity of the substance with iodoform was confirmed by comparing smell, colour and melting point. But the direct treatment cannot be used for the estimation of acetone in the compound since 2:6-dimethoxy quinone also yields some iodoform by similar treatment. Booth and Saunders[12] have observed that quinones in general give the iodoform reaction.

For estimating the acetone the following procedure was adopted. A known quanity of the addition compound was treated with sodium hydroxide solution and distilled. The liberated acetone was condensed and estimated according to the method of Houghton.[13] The percentage of acetone in the compound was found to be 21. $C_{11}H_{14}O_5$ requires acetone 25·7%. The low result seems to be due to the low recovery of acetone in the distillation process.

Condensation of 2:6-*dimethoxy quinone with methyl ethyl ketone*

Methyl ethyl ketone condensed with 2:6-dimethoxy quinone under the same conditions as acetone and gave a colourless substance melting at 131–32°. Its reactions and properties are similar to those of the acetone compound (Found: C, 60·4; H, 7·1; $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7%).

SUMMARY

In the presence of potassium carbonate or potash, acetone forms an addition product with 2: 6-dimethoxy quinone. Its properties and reactions are described. They give evidence for the presence of an aliphatic hydroxyl group and a ketone carbonyl. The combination is considered to involve addition of the acetone molecule at the C = O group in the 4-position of the quinone. Methyl ethyl ketone also forms a similar addition compound. Other simple *p*-benzoquinones do not give this type of compounds.

REFERENCES

1. Rao, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1948, 245.
2. Rothbaum, Ting and Robertson *J.C.S.*, 1948, 980.
3. Erdtman .. *Proc. Roy. Soc., London*, 1934, **143**, 181.
4. Bamberger .. *Ber.*, 1902, **35**, 1425.
5. Japp and Stratfield .. *J.C.S.*, 1882, **41**, 270.
6. ——— and Miller .. *Ibid.*, 1885, **47**, 11.
7. Staudinger .. *Ber.*, 1908, **41**, 1355.
8. Ismail .. *Nature*, 1949 **163**, 565.
9. *Pharmacopœia, U.S.*, 14th Edn., 1950, 336.
10. Baker *et al.* .. *J.C.S.*, 1941. 665.
11. Will .. *Ber.*, 1888, **21**, 612.
12. Booth and Saunders .. *Chem. and Ind.*, 1950, 824.
13. Houghton .. *Ind. Eng. Chem.* (*Anal. Edn.*), 1937, **9**, 167.

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